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MEMORIAL LECTURES

DELIVERED BEFORE

THE CHEMICAL SOCIETY,

1893–1900.

BY

Prof. J. W. MALLET.
Prof. T. E. THORPE.
Prof. P. T. CLEVE.
LORD PLAYFAIR.
Sir F. A. ABEL, Bt.
Dr. W. H. PERKIN.
Prof. H. E. ARMSTRONG.
Prof. G. F. FITZGERALD.
Prof. P. P. BEDSON.
Prof. P. F. FRANKLAND.
Prof. F. R. JAPP.
Sir H. E. ROSCOE.
Prof. J. M. CRAFTS.
Prof. O. PETTERSSON.

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J. S. Hall

STAS MEMORIAL LECTURE.*

(Delivered December 13, 1892.

Jean-Servais Stas, and the Measurement of the Relative Masses of the Atoms of the Chemical Elements.

By J. W. Mallet, F.R.S., Professor of Chemistry in the University of Virginia, U.S.N.A.

A meeting of the Chemical Society for the purpose of doing honour to the memory of Stas is a fitting expression of the admiration of British chemists for his scientific life and work.

At the desire of the Council of the Society conveyed by a letter from our Senior Secretary last summer, the writer of this paper undertook to prepare a notice of the investigations on the atomic masses of the elements, which will always remain most intimately associated with the name of the distinguished Belgian chemist—whose death, in ripe old age, was announced a year ago—and, in connection with his work, to review the general history and present state of our knowledge in regard to these most important of chemical constants.

Few chemists have better deserved than he to be held in honour by an assembly of chemists. Not for his contributions to descriptive chemistry in the discovery and examination of new substances, nor for

* Chemical Society's Memorial Lectures, No. 1. Compare Chemical Society's Proceedings, 1892, 203, where the discussion which took place on the occasion of the delivery of the lecture is reported. The original of the appended letter was addressed to Mr. Crookes.

his eminence as a teacher or a writer, nor for his practical applications of knowledge to the affairs of human life, is he chiefly remembered—though in all these directions his services claim honourable record in the history of our science—but especially will those who themselves cultivate this science ever think of him as the man who, with untiring patience and clear-sighted power of investigation, worked on for years upon the foundation stones of quantitative chemistry, thinking no pains too great, no toil too severe, that could render more accurate the results which others might take and trust as the basis of their researches—however little the greater part of mankind might feel interest in, or even know of, his quietly pursued investigations.

The simple story of his life has been gracefully told* by him who four months later was himself to be taken from among the living—by the great chemist for whom Germany and England are united in personal sorrow, and to whose pen we owe like biographies, clear, instructive and elegant, written in former years, of Dumas and Wurtz, Liebig and Wöhler, Kopp and Will.

Born at Louvain on the 21st of August, 1813, Stas, on growing up to manhood, had to make his own way in the world, entered upon and completed a course of study with a view to becoming a physician, and graduated as Doctor of Medicine, but does not seem to have long, if at all, pursued the practice of his profession. In association with his friend L. G. de Koninck he undertook, without access to any regularly equipped laboratory, in the attic of his father's house,† in 1835, the investigation of a crystallizable substance, phloridzin, which they extracted from the bark of the root of the apple tree, and this early research seems to have indicated or developed the taste for chemistry which determined the course of his after life. It also led to his attempt to secure a position in the laboratory of Dumas in Paris, one of the very few places in Europe where at that time practical instruction in chemistry, and the resources of a well equipped laboratory, were to be found. Evidence of the earnestness with which

* *Berichte d. deutsch. chem. Gesellschaft*, 25er Jahrg., No. 1, S.1. Other sketches of the life of Stas have also been published, as, for instance, in the *Revue de Belgique*, 15 Février, 1892 (by Prof. L. Errera of the University of Brussels), in the number of "Nature" for May 26, 1892, p. 81, and in the Journal of the American Chemical Society (of which he was an honorary member) for September, 1892, p. 173, the last of these written by Prof. Edw. W. Morley. The latest memoir to appear, and doubtless that in which biographical details of most authority are to be found, is the "*Notice sur la vie et les travaux de Jean-Servais Stas*," prepared for the Academy of Belgium by Prof. W. Spring of Liège.

† Prof. Errera was informed by Stas himself that he made with his own hands the balance used in this early research. The knife edges were of steel, the index was of glass, fastened on by means of sealing wax. The materials, all together, did not cost more than 5 francs, but the balance was accurate to a milligramme.

the young Belgian sought entrance among the pupils of Dumas is furnished by the amusing anecdote of his repeated calls at the house, and efforts to obtain speech with the busy teacher, met each time by a maid servant's stereotyped "not at home," until at last, tired of his importunity, or interested by his eagerness, she once more gave the usual answer in a loud voice, but indicated by a significant gesture of her finger the door of the room in which her master was to be found, and allowed Stas to make his way in by himself. Accepted as a student by Dumas, the young Belgian chemist set to work upon the phloridzin he had brought with him, made some analyses of it, and examined a number of its reactions. Though he did not establish the formula which is now accepted for this substance, he proved that on boiling with dilute acids it splits up into phloretin and glucose, and thus added another member to the then small, but now extensive, list of glucosides, to which salicin had recently been shown to belong by Piria, at that time also working as a pupil of Dumas. This first research made in Paris was noticed by Berzelius in his *Rapport annuel sur les progrès de la chimie* with praise and a prediction of future eminence for the author.

Soon afterwards Dumas and Stas together worked upon the reaction of a mixture of potash and lime upon various alcohols, ethers and esters of the fatty series, producing salts of formic, acetic and valerianic acids from the corresponding alcohols, establishing the identity of valerianic acid so obtained with that occurring free in the natural oil of valerian, confirming the views of Cahours and Dumas as to the true chemical nature of the amyl alcohol of fusel oil, preparing from it the corresponding aldehyde, and distinguishing acetone as not belonging to the class of alcohols.

The relation between the fatty alcohols and acids was also exhibited in reference to ethal or cetyl alcohol from spermaceti.

In the same year Dumas and Stas also began together the important re-determination of the atomic mass of carbon which became the starting point of the long train of research which Stas made so peculiarly his own. The fact having been noticed, by Liebig and others as well as by Dumas, that in analyses of hydrocarbons rich in carbon—made by the combustion process, and free from all known sources of error—it not seldom occurred that the sum of the carbon and hydrogen found, as calculated from the carbon dioxide and water weighed, was greater than the quantity of the material analyzed, Dumas became convinced that the accepted views of the composition of carbon dioxide, or water, or both, must involve some error in regard to the relative weights of the elements concerned. The high and highly deserved reputation of Berzelius for accuracy, never before surpassed in quantitative determinations, demanded extraordinary

care on the part of any one who should call in question the numbers accepted on his authority, *viz.* :—

		On the hydrogen standard.
$C : {}_2O = 76{\cdot}432 : 200$	or	$12{\cdot}246 : 32{\cdot}042$
${}_2H : O = 12{\cdot}484 : 100$	„	$2 : 16{\cdot}021$*

Unprecedented care, and the most elaborate precautions, *were* taken in the re-investigation of these ratios, that of carbon to oxygen in carbon dioxide by Dumas and Stas, and that of hydrogen to oxygen in water by the former, assisted by the latter in the preliminary part of the work. To determine the composition of carbon dioxide, carbon, taken in the several forms of graphite, natural and artificial, and in that of diamond, was burned in a porcelain tube in a current of purified and dried oxygen gas, and the carbon dioxide formed was absorbed by caustic potash and weighed, due account being taken of any ash left as a residue of the combustion. A number of carefully repeated experiments, affording closely accordant results, gave the mean value $C = 74{\cdot}956$ if $O = 100$; or $75{\cdot}005$, if the experiments with diamond carbon alone were considered, as the investigators inclined to place most confidence in these.

Soon after the completion of this research (in 1840) Stas left Paris, and returned to his own country to take up the duties of the professorship of chemistry in the *École Royale Militaire* at Brussels. In this position he lived and worked for more than a quarter of a century, receiving but a small salary, which was after a number of years increased on his petition ("with a view to the prosecution of his scientific work") by but the scanty sum of 200 francs a year—an increase which he declined to accept. He was finally, by an affection of the larynx and bronchial tubes which impeded his utterance, obliged to give up lecturing, and to offer his resignation before the end of the thirty years of service which would have entitled him to a pension.† He was then given a position in connection with the mint, as *Commissaire des monnaies* in the Treasury department of the Belgian Government, but did not long hold this office, as his sense of duty to the public forced him to actively oppose a project for coining a

* The wonderful accuracy of Berzelius' work generally is illustrated by the fact that this number becomes 15·894—almost exactly agreeing with the latest determinations of the present day—if the weighings of Dulong and Berzelius' three experiments on the synthesis of water be corrected for the buoyancy of the air, this correction not having been applied by these chemists themselves. (Letter from Dr. Clark read at meeting of Chemical Society, Nov. 16th, 1841—Phil. Mag. [3], **20**, 341.)

† His name appears in the *Comptes rendus* of the French Academy of Sciences for the 22nd of September, 1845, as "*professeur à l'École polytechnique de Bruxelles.*"

large amount of silver—as a speculation based upon the greatly reduced real value of the metal—and on the scheme being carried, as a result of a change in the Ministry in 1872, he at once resigned. He continued to live in Brussels to the end of his life, unmarried, and with simple surroundings, in the house No. 13, Rue de Joncker, in the Faubourg Saint-Gilles.

He was called to fill sundry honorary offices, becoming Vice-President of the Council of Public Health, Technical adviser of the National Bank, Permanent member of the Administrative Council of the University of Brussels, President of the Geological Map Commission, and of the Observatory Commission, Member of the Commission of Hygiene, and of the Statistical Bureau, an active Member of the International Committee of Weights and Measures, and a Member of one of the juries of the London International Exhibition of 1862. He received civic honours in various forms, being made Grand Officer of the Order of Leopold of Belgium, and of the French Legion of Honour, and a Knight of several other European orders.

In the world of science also he received numerous proofs of esteem and admiration—he was President of the Academy of Sciences of Belgium, a Corresponding Member of the French Academy of Sciences, a Foreign Member of the Royal Society of London, an Honorary Member of this Society and of the German Chemical Society—and of many other of the principal scientific societies of the world—he received honorary degrees from several Universities, and on various occasions medals were presented to him, notably the Davy Medal of the Royal Society in 1885, and in 1891 a medal struck to commemorate the fiftieth anniversary of his becoming a Member of the Royal Academy of Sciences of Brussels, this latter bearing as motto the not ungraceful play upon words—*Servatus Stas et usque in memoriâ stabis.*

On the occasion of this celebration of his scientific jubilee he received numerous addresses of congratulation, and a discourse upon his life and work was delivered by Professor W. Spring, who has, with M. Depaire, undertaken the task of preparing for publication the large mass of scientific material for further papers which Stas left behind him in manuscript.

By his independence of thought and boldness of utterance Stas incurred the enmity of the "clerical party" of Belgium, the journals representing which assailed him violently for the stand he took in behalf of freedom of investigation and freedom from church control in public teaching. The shadow of governmental disapproval was in some measure cast upon him by aspersions in the Belgian Chambers from the lips of members of the Ministry. But he was

amply sustained by the hearty approval of general public opinion in his native land.

Stas was "*libéral et libre-penseur*," even materialist in his views; he lived, died and desired to be buried outside the pale of the Catholic Church, yet was esteemed by and on terms of friendship with prominent men of the opposite camp, such as Montalembert, Father Secchi, Thonissen, Victor Jacobs, the canons Gilson and Van Weddingen, Mgr. Deheselle, Bishop of Namur, and many others.

He was strongly independent in character, yet he was the personal friend of some men high in political and social position, notably of the late Dom Pedro, Emperor of Brazil, and of Prince Jerôme Bonaparte, the latter of whom he used to call upon at the Palais Royal when, during the period of the Second Empire, he happened to be at Paris.

He was always ready with kindly encouragement and help for young men entering upon a scientific career, and quietly befriended many such, though he never allowed personal considerations to influence him to the detriment of the higher interests of science and his country. He rendered many services to those whom he liked, but men who knew him personally agree that towards those who incurred his displeasure he was merciless,—"*pour les intrigants et les demi-savants il était terrible.*" He did not readily accept the newer theories of modern chemistry, and indeed used to take pleasure in ridiculing some of them until a few years before his death, but it has been remarked with truth that he rendered one great service to the progress of the newer chemistry by the part he heartily took in helping forward Kekulé in the earlier years of his career.

He died on the 13th of December, 1891, and was followed to the grave by those who best knew him, with admiration for the faithful votary of science, and esteem for the personal worth of the upright man, who in all things had set before him as his chief aims truth and the freedom that the truth can give.

During the long period, more than half a century, of Stas' life in Brussels—a life of quiet, steady intellectual labour, not untroubled by worldly care—he carried out valuable researches in other directions than that of his specially-chosen investigation of atomic weights. In the domain of pure chemistry, he reported in 1842 to the French Academy of Sciences—at the same meeting at which was communicated Dumas' classic paper on the composition of water—the results of repeated analyses of atmospheric air made at Brussels for comparison with the results of similar analyses which had been recently made at Paris by Dumas and Boussingault. In the Royal Society's Catalogue of Scientific Papers there is noted the appearance in

1843 of a report by Stas and de Hemptinne on a memoir by Melsens in regard to the action of sulphuric acid on acetic acid. In 1847 he published in the *Annales de Chimie et de Physique* a paper on the properties and composition of acetal, which had been first prepared by Döbereiner and afterwards examined in an imperfectly purified condition by Liebig—Stas indicated a new method of preparation and the means of properly purifying the substance, made good analyses of it, determined its vapour density, and correctly established its molecular formula. In 1850 he sent to the French Academy of Sciences a note on the substances detected by him in the amniotic and allantoic fluids of different animals, a line of research which he does not seem to have followed up further.

In applied chemistry his work was important and marked by accuracy and thoroughness. In 1845 he sent to the Academy of Sciences at Paris a paper on the disease then affecting the potatoe crop in Belgium, in which he gave the results of his experiments on the chemical condition of the diseased tubers in comparison with those apparently healthy. In November, 1850, Count Hippolyte de Bocarmé murdered his brother-in-law, Gustave Fougnies, by the forcible administration of nicotine, which the criminal had learned to prepare, and had actually prepared for the purpose. The trial, in the following year, of the Count, and of his wife as accessory to the murder, excited great attention, both on account of the social prominence of the accused and the unusual form of the crime. Stas furnished clear and important evidence as to the identity of the poison used, and, in connection with his investigation of the case, devised the well-known general method for the detection of vegetable alkaloïds in cases of poisoning which is commonly referred to by his name in association with that of Otto, who afterwards suggested some modifications of it. For a report on the chemical section of the London International Exhibition of 1862, Stas examined the relative advantages of the older method of decomposing the fats by lime saponification, and the newer practice of using sulphuric acid to decompose such materials, and indicated the superiority of the latter process for the purpose of the manufacturer of candles. In the years 1877 to 1879, as a Member of the *Comité international des poids et mesures*, he took an active part, along with H. Sainte-Claire Deville, in the investigation of the properties of the metals of the platinum group, and the preliminary work relating to the production of the great ingots of iridio-platinum to be used in making the new international standards. It appears also that he conducted for the Belgian Government important investigations in regard to alloys for use in the construction of artillery, but the results have not been given to the public.

The great work of Stas' life, however—that on which he freely spent his time, his thought, his painstaking labour and no small share of his not too abundant private means—was, as has been said, the investigation of the atomic masses or weights of a number of the more important chemical elements. This work he entered upon as an independent study soon after his settlement in Brussels, apparently about 1842 or 1843, led to it by his interest in the share he had already taken in determining with Dumas the atomic weight of carbon, and by the desire expressed by his great master, as well as felt by himself, to apply methods of similar accuracy to a revision of the long-trusted numbers of Berzelius, and thus to lay the foundation securely for a discussion of any general principles connecting these constants, particularly the supposed multiple relation of all other atomic weights to that of hydrogen which had originated with Prout in the early part of the century.

In order to fairly consider the contributions to knowledge in this direction which we owe to Stas, it may be allowable to notice briefly the succession of fundamental ideas which have gradually led up to the question—What is the mass (or, less accurately expressed, the weight) of an atom of a particular chemical element?

In the first place *matter exists of different kinds, recognizable by difference in properties when examined under the same conditions.* This must have been noticed as soon as external nature became, even in the most general way, the subject of human observation.

Some masses of matter are homogeneous, or of the same kind throughout; others are heterogeneous, or of different kinds in different parts of the mass. Examples of fairly homogeneous or pure materials, such as gold, copper, water, and common salt, must have occasionally been in men's hands in prehistoric times, and a moderately long list of such substances, identified by recognized properties, and distinguished by special names, can be quoted from the days of Indian, Egyptian, Greek and Roman civilization. This list was no little added to by the labours of the middle age alchemists. For ages, however, numerous mixtures or impure substances were referred to and described on the same footing with pure materials, and substances altogether free from admixture were so seldom obtained that variability, to a greater or less extent, rather than invariability of properties seemed to be the rule in nature. Even in our own day how many men talk and think of glass, steel and other materials of variable properties as if they were homogeneous forms of matter. The retarding influence upon the progress of true knowledge exerted by confusion of thought in regard to pure substances and mixtures was very great. Even in and beyond the days of Cavendish and Priestly, when quantitative experiments began to be much attended

to, the fact that atmospheric air was found of constant, or nearly constant, composition, was long a stumbling block in the way of clear distinction between a homogeneous compound and a uniform mixture. Another fruitful source of obscurity in early chemical thought was the long prevalent confusion between the *constituents* and the *properties* of any given substance, confusion evinced by the terms sulphur, mercury, spirit, as used by alchemistic writers, and phlogiston later on, applied to things supposed to exist in or to be separable from the forms of matter under discussion. On this confusion, along with that in regard to pure and mixed substances, depended in large measure the early and long held belief in the transmutation of metals.

All the parts of a homogeneous or pure substance exhibit the same properties, and behave in the same way, when placed under the same external conditions. Although difference in properties or behaviour had in early times been often used to separate mixtures, and to isolate from them particular constituents, as in the distillation of strong alcohol from wine and the separation of silver from lead by cupellation, it seems to have been felt that these differences were rather of degree than of kind, and even so late as the first part of the eighteenth century the idea does not seem to have been quite clearly held and generally adopted that substances could be obtained which would no longer exhibit any such difference, but would show themselves invariable in properties and behaviour under the same conditions. Experiments that nowadays seem but laboriously useless, like Boerhave's thirty times repeated distillation of mercury, were valuable proofs of the truth in question.

Strictly homogeneous or pure substances are observed to become changed into new substances, with new properties, and these changes may be proved to depend on the union of forms of matter previously existing as distinct, or the separation of distinct substances from a previous condition of union—in a word, on combination or decomposition. Among the earliest chemists to grasp the idea of the continued existence of matter as to its mass, but with change of properties, seems to have been van Helmont, who clearly recognized copper and silver as present in solutions of their salts though these were quite unlike the metals themselves in properties. The term "spagiric art," applied to chemistry in the sixteenth century, to the latter part of which van Helmont belonged, indicated an appreciation of chemical change as due to combinations and decompositions, and this notion, coupled with that of the continued existence of matter though changed in character, substituted a true idea of transmutation for the older and looser one.

Pure substances, after having undergone chemical change, may be

recovered, qualitatively and quantitatively the same as they were at first, by a reverse process of change. To the labours of van Helmont, Boyle and Boerhave much credit is due for gradual advance toward the doctrine of the "conservation of matter"—many others of the earlier chemists added something to the evidence leading up to this truth—the discoveries of Black and Cavendish brought it further into view. But it assumed its due importance, and began to receive universal recognition with the constant appeal to the balance which Lavoisier made, and taught others to make.

Certain substances have resisted all attempts to decompose them, and in the present state of our knowledge are recognized as CHEMICAL ELEMENTS, *or the simplest distinct forms of matter.* Robert Boyle, in the middle of the seventeenth century, set forth this idea in a much more definite form than had presented itself to the earlier chemists, some of whom seem, however, to have had occasional glimpses of it; but it was first stated by Lavoisier, more than a hundred years later, with the peculiar intelligence and clearness which characterized his mode of thinking on chemical subjects. By the same line of reasoning wherewith he reversed the older way of looking at combustion, which the advocates of phlogiston had insisted on, he rendered clear the distinction between substances or kinds of matter and their properties, required the mass of reacting substances to be constantly kept in view, and gave the true grounds for distinguishing between elements and compounds. He said—"If we apply the term elements or principles of bodies, to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all the substances into which we are able to reduce bodies by decomposition. Not that we are entitled to affirm, that these substances which we consider as simple, may not themselves be compounded of two, or even of a greater number of more simple principles; but since these principles cannot be separated, or rather since we have not hitherto discovered the means of separating them, they act with regard to us as simple substances, and we ought never to suppose them compounded until experiment and observation have proved them to be so." The brilliant researches of Davy, "proving by experiment and observation" the compound nature of the alkalis and earths, and e evidence which he brought forward to establish the elementary character of chlorine, probably contributed more than anything else to permanently fix, in the early part of the present century, in the minds of all chemists the distinction, and the means of discriminating, between elements and compounds.

These elements, as also the compounds to which they give rise, combine with each other only in certain fixed proportions by weight.

With the more general use of the balance in the investigation of chemical changes, which attended the overthrow of the phlogistic theory, came a comparison of the quantities of different substances, at first chiefly the then known acids and bases, which would enter into combination with each other. In the establishment of the fact that such combination, unlike mere mixture, always requires the use of the same substances in the same proportion by weight in order to form the same homogeneous product, the names of Wenzel, Richter, Fischer and Proust deserve prominent mention. Especially important was the discovery by Wenzel and Richter that, when two neutral salts mutually decompose each other, both the two resulting salts are also neutral, so that the quantities of the constituents which replace each other are "equivalent" each to the other. This showed the possibility of determining by experiment the several quantities of a number of different acids which would neutralize a fixed amount of a single base, then the several quantities of a number of bases which would neutralize a fixed amount of a single acid, and from the results of these experiments deducing the relative quantities of any acid and any base in the list which would just satisfy each other in combination. The views of Berthollet, in regard to the influence upon combining proportions of the larger or smaller masses of the several substances presented to each other for reaction, have, with a different interpretation, received in much later times the recognition due to the real importance of the facts he studied, but in his own day they exerted a retarding influence upon the spread of the doctrine of combination in definite proportions.

In different compounds consisting of the same constituents, for a fixed quantity of one constituent the different quantities of another constituent bear to each other a simple multiple or sub-multiple relation. That this is true in certain cases had been observed by Proust, in the course of his controversy with Berthollet as to the fixedness of combining proportions, and probably the cases instanced may have contributed to the impression made on Dalton's mind by his own observations on the different proportions in which carbon was known to unite with hydrogen and with oxygen respectively, but to the latter belongs without dispute the honour of announcing the principle as a general one, and of basing upon it a true chemical "atomic theory" of the nature of matter, substituting a definite theory which could be tested by quantitative experiment for the more or less vague and speculative ideas in regard to atoms which had come down from Leukippos and Lucretius, from Boyle and from Boscovich. A little later, Wollaston and Thomson supplied additional evidence in support of the "law of multiples" by experiments on the neutral and acid carbonates and oxalates.

By rationally founded supposition we may assume each pure substance to be made up of minute particles, of uniform and constant mass, in which particles reside all properties of the substance save those (such as physical state—solid, liquid or gaseous—and crystalline structure) which depend upon cohesion. In putting forth for the first time in fully published form* his new views of the relation to chemical facts of a corpuscular theory of matter, Dalton used the term "ultimate particles," and distinguished between a "compound particle" and the "simple elementary particles" of which it consists. In reference to compound substances Berzelius employed the term "compound atom," and Thomson the term "integrant particle." Avogadro distinguished "*molécules intégrantes*" and "*molécules élémentaires.*" Much credit belongs to Laurent at a much later day for rendering common the use of the word "molecule" to signify an ultimate particle of any substance, elementary or compound, in which the identity of the substance is retained, and for clearly distinguishing between the molecule and its constituent atoms, the latter similar to each other in the case of an element, dissimilar in that of a compound.

The relation between the weights of the different constituent elements in a compound represents the relation between the weights of the larger or smaller aggregates of atoms of the several different kinds which make up the molecule. The determination of the relative combining weights of the various elements calls for the application, with the greatest possible accuracy, of the processes of chemical analysis. To a large extent the development and improvement of these processes were in the early years of the present century brought about by the patient and intelligent efforts of Berzelius to ascertain the combining weights of the elements.† With apparatus in many respects inferior to that

* John Dalton—a new system of Chemical Philosophy, Part I., Manchester, 1808, p. 213. Dr. Thos. Thomson recorded in his journal the 26th August, 1804, as the date on which he heard privately from Dalton a statement of his views. Dalton's preface indicates that "In 1803, he was gradually led to those primary laws, which seem to obtain in regard to heat, and to chemical combinations, and which it is the object of the present work to exhibit and elucidate. A brief outline of them was first publicly given the ensuing winter in a course of lectures on Natural Philosophy, at the Royal Institution in London, and was left for publication in the Journals of the Institution; but he is not informed whether that was done."

† Berzelius began work in this direction in 1807, his attention having been attracted by Richter's investigations, but soon afterwards he became acquainted with Dalton's new atomic theory of the nature of combination, and appears to have been at once impressed with its great importance, and at the same time with the need of more exact experimental data for its support and development. His "*Essai sur la théorie des proportions chimiques*" is said to have been published in Swedish in 1814, in French in 1819, and in German translation in 1820. In an article, in Thomson's Annals of Philosophy, Vol. II., July to December, 1813,

of the present day, and with scarcely any aid from chemical manufacturers in preparing pure materials and reagents, but with unsurpassed manipulative skill, and the most honest criticism of his own work and endeavour to improve its accuracy, he produced the first fairly trustworthy list of numbers representing the proportions by weight in which the elements combine. Many other chemists have since worked in the same field, but the most worthy successor of Berzelius in such labours has unquestionably been Stas. With greatly better resources in the way both of apparatus and material, with equal earnestness in seeking for the truth, with equal intelligence and skill, he took up the task which became that of the largest part of his scientific life, and for a more limited list of elements than Berzelius had investigated produced results of a degree of accuracy which, it is high praise to say, would have delighted no one more than Berzelius himself, could he have known of them and of the methods by which they were reached.

If the mass (or weight) of a single molecule of a compound can be ascertained, in terms of the mass of an atom of some particular element adopted as the unit of measurement, and the relative masses of the aggregates of atoms of the different constituents be deduced from the combining weights of these constituents, it needs only that the number of atoms going to make up each such aggregate be ascertained in order to learn the mass (or weight) of each elementary atom in terms of the unit adopted. Dalton at first adopted purely conjectural rules in regard to the numbers of atoms combining with each other, thus :—

"1. When only one combination of two bodies can be obtained, it

entitled "Essay on the Cause of Chemical Proportions"—an article which does not seem to have been much noticed, and which it would be interesting to compare with the Swedish Essay of 1814—Berzelius thus expresses himself (pp. 453, 454)—"As far as I know the English chemists Dalton, Davy, and Young, are the only persons who have yet attempted to make these determinations; and they have proceeded in a manner somewhat different. Mr. Dalton, to whom the honour of the first attempt is due, has endeavoured to determine the relative weights both of simple and compound atoms. (*New System of Chemical Philosophy.*) Davy, though he has not adopted the atomic theory of Dalton, has embraced the doctrine of definite proportions; and what Dalton calls an atom, he calls a proportion. (*Elements of Chemical Philosophy.*) Dr. Young, in his *Introduction to Medical Literature*, has made similar determinations; but what Davy calls *proportion*, Young calls *combining weight*. But none of these philosophers have attempted to give any great degree of exactness to their determinations. They have frequently even omitted stating the experiments from which these determinations are derived. The method which they have adopted of giving round numbers, though it facilitates the recollection and calculation, is scarcely consistent with the object of scientific researches, and ought to be rejected: for even supposing that perfect exactness could never be obtained, it is nevertheless the object towards which all our efforts should be directed."

must be presumed to be a binary one, unless some cause appear to the contrary.

2. When two combinations are observed, they must be presumed to be a binary and a ternary.

3. When three combinations are obtained, we may expect one to be a binary, and the other two ternary," &c.

These terms being thus explained,

1 atom of A + 1 atom of B = 1 atom of C, binary.
1 atom of A + 2 atoms of B = 1 atom of D, ternary.
2 atoms of A + 1 atom of B = 1 atom of E, ternary," &c.

These rules had no experimental evidence whatever to support them, and merely aimed at the greatest possible simplicity in the assumptions made. They have often been quoted with unfavourable criticism, but it is not so often noticed that later on Dalton himself saw the weakness of such arbitrary rules. In the second volume (Part I.) of his "New System of Chemical Philosophy," pp. 349, 350, he says:—

"When two bodies, A and B, combine in multiple proportions; for instance, 10 parts of A combine with 7 of B, to form one compound, and with 14 to form another, we are directed by some authors to take the smallest combining proportion of one body as representative of the elementary particle or atom of that body. Now it must be obvious to anyone of common reflection, that such a rule will be more frequently wrong than right. For, by the above rule, we must consider the first of the combinations as containing 1 atom of B and the second as containing 2 atoms of B, with 1 atom or more of A; whereas it is equally probable by the same rule, that the compounds may be 2 atoms of A to 1 of B, and 1 atom of A to 1 of B respectively; for, the proportions being 10 A to 7 B (or, which is the same ratio, 20 A to 14 B), and 10 A to 14 B; it is clear by the rule, that when the numbers are thus stated, we must consider the former combination as composed of 2 atoms of A, and the latter of 1 atom of A, united to 1 or more of B. Thus there would be an equal chance for right or wrong. But it is possible that 10 of A, and 7 of B, may correspond to 1 atom A and 2 atoms B; and then 10 of A, and 14 of B, must represent 1 atom A, and 4 atoms B. Thus it appears the rule will be more frequently wrong than right.

It is necessary not only to consider the combinations of A with B, but also those of A with C, D, E, &c., before we can have good reason to be satisfied with our determinations as to the number of atoms which enter into the various compounds."

The true foundation for determination of molecular mass, and of the numbers of atoms going to form particular molecules, was laid by

Gay Lussac's memorable research* (published in the same year with the first part of Dalton's "New System") on the proportions by *volume* in which gases combine,† and the important hypothesis of Avogadro (put forth three years later, in 1811) that all gases under like physical conditions contain in equal volumes equal numbers of molecules. But half a century or more had to pass before the confusion was fairly got rid of between molecule and atom, between equivalent and atomic weight. Gradually more and more light was shed upon the definition and the constitution of the molecule, and its relation to its constituent atoms, by the studies of Dulong and Petit upon specific heat, of Mitscherlich upon isomorphism, of Faraday upon electrolysis, of Liebig and Wöhler upon isomerism, of Dumas, Laurent and Gerhardt upon substitution, of Frankland upon valence. Most of all we are indebted to Cannizzaro for concentrating this light, and clearing up the indistinctness of ideas and of language which lingered in the chemical world up to the time of his discussion, in 1858, of the true methods of determining molecular and atomic weights.

It is not necessary, in reviewing the work of Stas, to discuss the steps in detail by which, various possible multiple values for an atomic weight having been ascertained by experiment, it has been settled how we are to decide between these. This was not the line of enquiry with which Stas identified himself. Indeed, the principles to be applied had been fairly worked out, and Cannizzaro's statement of them was before the world, when the first great memoir of the Belgian chemist was published. His efforts were aimed at the improvement of methods of experiment, and their application, with the utmost attainable accuracy, so as to secure results, in the form of experimental data as to combining weights, which should be entitled to the highest confidence.

That the ascertainment with precision of the masses of the atoms

* Preceded by the publication in 1805 of the results as to the volume relations of oxygen and hydrogen observed by Gay Lussac and v. Humboldt.

† It is curious to notice the considerable mutual distrust of Dalton and Gay Lussac for each other's conclusions, when in fact each was supplying the most weighty evidence in support of the doctrine of the other.

A noteworthy passage occurs on p. 556 of Part II. of Dalton's "New System," published in 1810, the year before the announcement of "the law of Avogadro." Speaking of Gay Lussac's views, he says "In fact, his notion of measures is analogous to mine of atoms; and if it could be proved that all elastic fluids have the same number of atoms in the same volume, or numbers that are as 1, 2, 3, &c., the two hypotheses would be the same, except that mine is universal and his applies only to elastic fluids. Gay Lussac could not but see (page 188, Part I. of this work) that a similar hypothesis had been entertained by me, and abandoned as untenable; however, as he has revived the notion, I shall make a few observations upon it, though I do not doubt but he will soon see its inadequacy."

of the elements was an object worthy of the consecration of so many years of labour as Stas bestowed upon it, may well be admitted if we reflect how completely the atomic theory has become bound up with the whole of chemical philosophy, how fruitful it has been of new discoveries, how much we may yet hope for from its consolidation and development, what nobility and dignity it has given to chemistry as a part of human knowledge. By the chemist at his balance the arm of reason is directed into those regions of almost inconceivable minuteness, which lie as far beyond the reach of the most powerful microscope as that carries us beyond the reach of the naked eye, quite as impressively as that same arm is stretched forth by the astronomer at his divided circle to reach and to weigh the mighty planets that shine in the remotest regions of our solar system.

Early History of Investigation as to the Atomic Weights of the Elements.

The determination of atomic weights dates, of course, from the publication of Dalton's theory; the earlier ascertainment of certain individual combining proportions, by Richter, Proust and others, are not properly to be taken account of under this head.

The atomic weights originally set forth by Dalton himself were only very rough approximations, based upon the adoption of the hydrogen atom as the unit, the arbitrary assumptions, already alluded to, of the *numbers* of atoms combining, and the results of such analyses of known compounds as he could command. Some of these analyses were made by himself, many of them by other chemists. Thus we find, for example—

	Relative weights of the ultimate particles.	
	New system, Part I. 1808.	New system, Part II. 1810.
Hydrogen	1	1
Oxygen	7	7
Azote	5	5
Carbone	5	5·4
Sulphur	13	13
Phosphorus	9	9
Iron	38	50
Copper	56	56

Berzelius began his experiments on combining proportions in 1807, and a year or two later under the stimulus of the new views

of Dalton,* gave himself up in large measure to the extension of these experiments, which developed into his great work on atomic weights.† He says himself‡—"*L'étude de ces phénomènes*" (the decomposition of the alkalis in Davy's hands, and an apparently parallel decomposition of ammonia, by the electric pile) "*devait donc faire partie de mes expériences; et lorsque j'eus connaissance des idées de Dalton sur les proportions multiples, je trouvai dans le nombre des analyses, dont j'avais déjà les résultats, une telle confirmation de cette théorie, que je ne pus m'empêcher d'examiner lesdits phénomènes: et ce fut ainsi que le plan de mon travail sur une partie d'abord très-limitée des proportions chimiques, s'agrandit de plus en plus, et embrassa finalement les proportions dans toute leur étendue, dont j'étais loin de me faire une juste idée en commençant mes expériences. Elles donnèrent d'abord des résultats bien différens de ceux auxquels je croyais devoir m'attendre. A force de les répéter et d'y employer des méthodes variées, je m'aperçus des fautes commises. Eclairé par l'expérience de mes propres erreurs, et à l'aide de meilleurs procédés, je parvins à trouver une grande correspondance entre le résultat des analyses et les calculs de la théorie. La comparaison de ces résultats développa successivement de nouvelles vues, qui demandaient à être vérifiées, en sorte que le travail augmenta d'étendue et peut-être aussi d'importance.*"

Berzelius expressed his atomic weights in terms of that of oxygen, represented by 100, giving as his reasons for preferring this standard to that of hydrogen taken as unity, that most of the substances with which chemists were concerned were oxides or compounds of oxides, and that calculation was simplified by having multiples of 100 to re-

* In the early part of his first paper ("*Essais sur les proportions déterminées*," *&c.—Annales de Chimie*, **78**, 8) he uses this strong language in reference to Dalton's theory of combination in multiple proportions—"*Cette manière d'envisager les combinaisons des corps répand déjà au premier coup-d'œil une telle clarté sur la doctrine des affinités, qu'elle peut être regardée comme le plus grand pas qu'a fait la chimie vers son perfectionnement comme science, si l'hypothèse de Dalton peut être prouvée.*"

† The first publication of his analytical results was in 1810—"Försök rörande de bestämda proportioner, hvari den oorganiska Naturens beståndsdelar finnas forenada"—Hisinger and Berzelius; *Afhandlingar i Fysik, Kemi, och Mineralogie* III (1810), 162. In the *Annales de Chimie*, beginning with the No. for the 30th of April, 1811, and running through the volumes **78** to **83**, inclusive, appeared his "*Essais sur les proportions déterminées dans lesquelles se trouvent réunis les élémens de la nature inorganique.*" (*Traduit du suédois.*) Further papers on the same subject appeared for many years afterwards. His "Essay on the cause of chemical proportions, and on some circumstances relating to them; together with a short and easy method of expressing them," was published in Thomson's Annals of Philosophy for 1813. His "*Nouvelles recherches sur les proportions chimiques*" appeared in the *Annales de Chimie* for 1817.

‡ *Traité de Chimie, trad. par M. Esslinger.* Bruxelles, 1835. T. **4**, p. 533.

present the various numbers of atoms of oxygen. He conscientiously reported the actual weighings of his analyses, and along with them the results of some work by other chemists. He substituted more rationally founded rules for determining the numbers of the atoms in a compound for those arbitrarily adopted by Dalton, laying the greatest stress on proportions by volume in the gaseous state, and carefully examining the nature of the multiple relations in each series of compounds formed by the same elements. Taking into account the limited laboratory resources of the analytical chemist when Berzelius did most of his work, this work will always excite the admiration of those acquainted by experience with the difficulties he encountered, and will be the more admired the more closely it is examined, and the more fully it is seen how far the difficulties were surmounted. His results were not without some errors, which remained for correction by his successors—one of the most remarkable cases being that of the atomic weight of carbon, the revision of which by Dumas and Stas has been already spoken of, but it is not so remarkable that there were errors as that these errors were on the whole so few and of such relatively small importance.

Sir Humphry Davy, in his "Elements of Chemical Philosophy," published in 1812, gave what were in reality a number of atomic weight determinations, though he cautiously avoided the use of the word "atoms," and preferred to speak only of "proportions." He quotes results obtained by others, but bases his "proportions" largely on experiments made by himself and his brother, John Davy. He says—"I have in a few instances only given an account of the experiments, from the results of which the numbers representing the undecomposed bodies were calculated.

"To have given accurate histories of those experiments, would have been incompatible with the object of an elementary book devoted to the general truths and methods of the science; I shall however shortly present them to the public, in a work containing the details of labours that I have carried on during the last twelve years in analytical chemistry.

"I have usually given whole numbers, taking away or adding fractional parts, that they may be more easily retained in the memory. When the number was gained from experiments in which a loss might be supposed, I have added fractional parts, so as to make a whole number."

His numbers, therefore, were, like those of Dalton, approximations only, though better than those of Dalton. For example, he assumed

Hydrogen	1
Oxygen	15

Nitrogen	26
Carbon	11·4
Sulphur	30
Phosphorus	20
Iron	103
Copper	120

Some of these numbers are of course approximate multiples (that for phosphorus a sub-multiple) of the corresponding numbers now accepted.

In 1825 Dr. Thos. Thomson, of Glasgow, published in two volumes, his work entitled "An attempt to establish the first principles of Chemistry by experiment," of which he says in the preface that he had begun the laboratory experiments in the summer of 1819, and that they had occupied all his time, not taken up by the duties of his professorship, for five years. This book, which for a time attracted much attention, especially in England, has long since dropped out of notice on account of the atomic weights adopted in it having been proved to be seriously erroneous, and it has been held to reflect positive discredit on the author. Never has a more severe criticism been passed by competent authority upon any scientific work than that of Berzelius upon this one. In the German edition of his *Jahresbericht* for 1827, *S.* 77, he says "*Diese Arbeit gehört zu den wenigen, wovon die Wissenschaft auch gar keinen Gewinn hat; mehreres in dem experimentalen Theile darin, ja sogar mehreres von dem Grundversuchen selbst, scheint nur am Schreibtische ausgearbeitet worden zu sein, und die grösste Höflichkeit, welche die Mitwelt dem Verfasser erweisen kann, ist, diese Arbeit als nie herausgekommen zu betrachten.*" This amounts to a charge of stating as the results of experiments, reported as actually made, figures which had simply been calculated out in advance to support a set of preconceived ideas —a charge so grave as not to be admitted except under the compulsion of proof. A pretty careful examination of the book, made with the desire to find, if possible, some less discreditable explanation of the erroneous results, yields the following conclusions. While the individual statements are clear, the relation between those in different parts of the work is in many cases confused, not seldom seeming to involve "reasoning in a circle." Thus in one place under the head of "Atomic Weight of Sulphur," we find the statement—"Hence sulphate of barytes is composed of

Barytes	9·75
Sulphuric acid	5
	14·75

The salt being neutral, and 9·75 representing an atom of barytes, 5 must represent the atomic weight of sulphuric acid." (Vol. **1**, p. 211.)

And elsewhere, under the head or "Atomic Weight of Barium," "It has been already explained, that sulphate of barytes is a compound of

Sulphuric acid.....	5
Barytes.....	9·75
	14·75

From which it is obvious, that 9·75 must be the atomic weight of barytes." (Vol. **1**, pp. 267, 268.) Other data are, however, also used to establish these same atomic weights. Thomson preferred to state all his atomic weights with reference to that of oxygen taken as unity, and, disentangling the chain of relations employed, we find it in the main to be made up of the following links. Assuming that air had been proved to consist of 20 per cent. of oxygen and 80 per cent. of nitrogen, and calculating from the average of several determinations of the density of oxygen as compared with that of air, he concluded that it should be represented by 1·1111. He took the density of hydrogen as 0·0694, and from these numbers deduced the atomic weight of hydrogen = 0·125. He says that he took the specific gravity of chlorine three times successively, and found it always 2·500 (air = 1)—hence he found chlorine to be 36 times heavier than hydrogen $\left(\frac{2{\cdot}5000}{{\cdot}0694}\right)$, and from this he calculated the atomic weight of chlorine = 4·5 (oxygen = 1), since 1 : 36 : : ·125 : 4·5. This made the weight of "1 atom muriatic acid = 4·625" (4·5 + ·125), with which he found 9·75 of barium oxide to combine, so that "1 atom barytes = 9·75," and "an integrant particle of anhydrous muriate of barytes weighs 14·375" (4·625 + 9·75). Heating to redness this muriate of barytes it lost the hydrogen of its acid and oxygen of its base, united to form water, and hence, subtracting 1 atom water = 1·125, he found "1 atom chloride of barium = 13·25" (14·375 − 1·125). A large proportion of his other atomic weight determinations turned upon the precipitation of a sulphate in solution by chloride of barium, the residual clear solution from which barium sulphate had precipitated being tested and found free from any excess of either barium or a sulphate, and he states in each case the weight of the original sulphate required for this exact equivalence with 13·25 grains of barium chloride. It is evident that the numbers assumed for chlorine and for barium chloride were too high. The reaction so largely made use of was moreover affected by error due to barium sulphate,

in precipitating, carrying down with it soluble salts, including soluble sulphates—a fact which was pointed out by Turner some years later as vitiating Thomson's results. In some cases the errors are probably traceable to the use of salts containing water of crystallization, the method of drying employed not securing the sharp separation of this from hygrometric moisture—this is observable in some experiments made in a similar way by J. Prideaux, who believed that his results supported those of Thomson (Phil. Mag., **7**, 1830, 276). But the chief source of error seems to have been that in the *preliminary* experiments, to ascertain the exact quantities of two salts which should just suffice for mutual decomposition, of none of which are the results recorded, but only the quantities finally ascertained,* Thomson must have been satisfied with only very moderate accordance between the figures of individual experiments, and have accepted the mean of these as exact, without thought for the large probable error involved—then, reducing his figures to correspond with the standard assumed, namely oxygen as unity, and expressing the results in *grains* he had but small quantities to work with in the final experiments which he does report, and the absolute errors are seemingly but very small. Thus, in his analysis of sulphate of zinc, which he himself speaks of as constituting in some measure the foundation of his whole superstructure, he says that he found 18·125 grains of the crystallized salt to be exactly precipitated by 13·25 grains of chloride of barium—the latter number, if calculated from our best ascertained atomic weights of the present day, should have been 13·14 grains; a difference of 11 hundredths of a grain.† That Thomson was influenced in no small degree in his selection of results, and his "rounding off" of numbers, by his prepossession in favour of the hypothesis of Prout there can be no doubt—an example is furnished by his discussion of the atomic weight of potassium as based upon the experiments of Gay Lussac and Thénard, and those of Berzelius, on the quantity of hydrogen set free from water by a

* Thomson says in his preface—"The work which I now present to the public contains the results of many thousand experiments, conducted with as much care and precision as it was in my power to employ." And at the end of his analysis of sulphate of zinc—"So that 18·125 is the weight of an integrant particle of the crystallized salt. It was the knowledge of this that induced me to make choice of 18·125 grains of the salt. My first experiments were made upon a much larger quantity; but I have often repeated them with 18·125 grains, and obtained the result just stated."

† Recently published experiments have shown that the production of a visible precipitate by the interaction of barium chloride and a soluble sulphate is not, in dilute solutions, a reaction of such great delicacy as has been often supposed. So that Thomson may have failed to detect small residues remaining in solution after his precipitations.

given quantity of the metal; in summing up he says of Berzelius' result, "This determination is a little below the truth, while that of the French chemists is a little above it. The mean of the two" (5·121 and 4·889) "gives 5·005 for the atomic weight of potassium. The true weight is undoubtedly 5." But, bearing in mind the means available for analytical work at the time, the average degree of accuracy which most analyses then represented, and the fact that even Berzelius himself long clung to and defended his value for the atomic weight of carbon, = 76·438 (instead of 75·02, as we should now take it), we should hesitate to believe in the truth of the imputation that results for experiments were deliberately *invented*.

The researches on atomic weights which have been so far noticed were the most important of those carried out and published in the early days of the chemical atomic theory—*i.e.*, up to the year 1820. Some individual results, however, and especially some most valuable physical determinations in respect to gaseous substances, were in the same period contributed by Gay Lussac and v. Humboldt, Biot and Arago, Dulong, Thénard, V. Rose, Chenevix, Marcet, Prout, G. G. Gmelin, and Sefström. Dulong and Petit's measurements of specific heats belong to the same period (1817–1819).

Atomic Weight determinations from the time of Berzelius to that of Stas.

Within this period—from 1820 to 1860, the year of the appearance of Stas' first great paper—the investigations of greatest extent in regard to atomic weights were those of—

E. Turner	1829–1833 (at. wt. of Mn previously determined, in 1818).
F. Penny	1839.
O. L. Erdmann and R. F. Marchand	1841–1852.
C. Marignac	1842–1858 (with further researches in much later years).
J. Pelouze	1845–1847.
R. Schneider	1850–1859.
J. B. Dumas	1859 (previous determinations for Ca and O in 1842, and (with Stas' aid) for C in 1840).

Turner's work was in large measure intended to clear up the discrepancy between the numbers for certain atomic weights which had been given by Berzelius and Thomson respectively. Turner introduced the practice of correcting his weighings for the buoyancy

of the air. Dumas began with the re-examination of carbon, as has been noticed, and seems to have become impressed, by the correction of Berzelius' number for this element, with the idea that the whole list of atomic weights needed revision, a work which, once entered upon, occupied him for many years, the great bulk of his results being published together in 1859. Although Dumas' results were far more correct than those of Thomson, the constant error connected with the precipitation of sulphates by barium chloride in the hands of the last named chemist was to some extent paralleled by defects in connection with the precipitation of chlorides by silver nitrate as largely practised by Dumas—each case teaches the lesson that the conditions affecting a reaction should be most carefully studied before it is applied to the determination of an atomic weight. Dumas' results for the atomic weights of carbon and of oxygen—the first that he obtained—are probably better than any of those he obtained afterwards. Penny's work was marked by care and intelligence in very high degree; he deserves to be considered a worthy fore-runner of Stas. Erdmann and Marchand, and still more Marignac, contributed a large number of carefully worked out results, including some of fundamental importance. Schneider bestowed special pains on the purification of the materials used, and Pelouze introduced important improvements in regard to the volumetric use of silver solutions.

Beside these more extensive researches, others of more restricted scope—many of them limited to the determination of a single atomic weight—were published during the period in question. Omitting a few papers of manifestly little value, the following list is presented in chronological order:—

F. Stromeyer	1816–26	J. Javal	1821
J. A. Arfvedson	1824–29	E. Rothoff	1826
A. J. Balard	1826	J. Liebig	1826
W. Hisinger	1826	E. Mitscherlich and Nitzsch.	1827
C. Löwig	1829	R. Hermann	1829–61
C. G. Mosander	1830–43	W. W. Mather	1835
R. Hagen	1839	R. Phillips	1839
J. Liebig and Redtenbacher	1841	H. Capitaine	1841
S. Baup	1841	V. Awdejew	1842
A. Beringer	1842	F. V. Wrede	1842
E. Péligot	1842–46	C. Rammelsberg	1842–59
V. A. Jacquelain	1842–51	J. J. Ebelmen	1842
L. Svanberg	1842–43	L. A. Salvétat	1843
E. Millon	1843–45	T. Anderson	1843
J. Wertheim	1843	H. Wackenroder	1844
E. Frémy	1844	P. A. Favre	1844
A. Erdmann	1844	L. Svanberg and Norlin	1844
C. E. Claus	1845	N. J. Berlin	1846–63
Th. Scheerer	1846–58	Faget	1846

E. J. Maumené	1846–50	C. Gerhardt	1846
I. Pierre	1847	Quintus Icilius	1847
A. Moberg	1848	L. Svanberg and H. Struve	1848
L. Svanberg and O. Nordenfeldt	1848	A. Laurent	1849
P. Louyet	1849	P. Einbrodt	1849
G. J. Mulder	1849	A. Demoly	1849
J. Lefort	1850	A. Levol	1850
L. E. Rivot	1850	R. F. Marchand and Th. Scheerer	1850
H. Struve	1851	F. Sacc	1851
A. Schrötter	1851	R. F. Marchand	1851
J. B. V. Borck	1851	J. F. Bahr	1852
T. Andrews	1852	R. Wildenstein	1853
T. Kjerulf	1853	J. Weeren	1854
F. Kessler	1855–61	H. Rose	1856–58
H. Ste. Claire Deville	1856–59	T. R. Weber (with H. Rose)	1856
J. W. Mallet	1856–59	W. P. Dexter	1857
K. V. Hauer	1857–58	A. Riche	1857
C. Tissier	1858	R. Bunsen and J. Jegel	1858
C. L. Vlaanderen	1858	M. Holzmann	1858
W. Wallace	1859	Rawack	1859
S. de Luca	1860	E. Lenssen	1860
		F. A. Bernoulli	1860

During the same period there were also published important investigations of a physical character bearing upon the determination of atomic weights. Of these by far the most valuable for this purpose were Regnault's researches on the densities of the principal gases (1845–1861). His work also on specific heats (1840–1861), and that of Kopp in the same direction (1848–1865) may be mentioned, although not affecting atomic weights in regard to their exact values.

Stas' Determinations of Atomic Weights.

In carrying out the researches on this subject to which Stas devoted most of the time at his command for more than forty years, he aimed at the determination, with greater precision than anyone before him had attained, of the atomic weights of some ten or twelve of the elements.

But he also aimed beyond this. He endeavoured, by so determining these constants, to settle several general questions of the most fundamental importance in regard to matter as studied by the chemist.

In the first place,—Is the mass or weight of an atom of a given element an absolutely constant quantity, so that chemical analysis, properly conducted, must always produce, from each substance examined, strictly the same relative quantities of the same constituents separated? Although this has generally been assumed as true beyond dispute since the early part of the present century, it has

occasionally been called in question, or some degree of doubt expressed in regard to it. Marignac was apparently the first chemist of recent times to suggest any doubt as to the constancy of combining proportions.* Stas himself considered the question as one requiring examination.† In 1883 Schützenberger and Butlerow published papers ‡ in which were reported certain anomalies in the results of analysis, believed not to be due to defective work, and for which these chemists suggested as a possible explanation the variation, within small limits, of the atomic weights of the elements concerned, so that the numbers representing these might depend in some small degree upon special physical conditions, as of temperature or pressure, or might vary for the same element as it entered into combination with different other elements. This last idea savours of the old views assuming the indefinite divisibility of matter, and is incompatible with the very essence of the Daltonian atomic theory. In a form more consonant with this theory Crookes has said§— "It may well be questioned whether there is an absolute uniformity in the mass of every ultimate atom of the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic weights of the atoms vary within certain narrow limits." "I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. We are here reminded of Newton's 'old worn particles.'" Dr. E. Vogel, of Alameda, California, has distinctly advocated || the idea of variability in atomic weights, and has endeavoured by a discussion of the results of Stas and others to find evidence in support of his thesis. Anyone who reflects upon the accumulation of facts tending to establish the atomic theory of the present day, in its commonly accepted form, will be apt to demand very clear proof of any such variability in atomic weights, will be inclined to consider mass as the most important means of identification for atoms of a definite kind, and will be likely to attribute the anomalies which have been pointed out in analytical results either to unnoticed errors of experiment, or to the assumption that in a reaction, supposed to be simple and definite, a few atoms may form compounds of a different order from the rest, and the resulting excep-

* *Archives des sciences physiques et naturelles*, 1860.

† *Mémoires de l'Académie Royale de Belgique*, **35**, 3 to 7.

‡ *Bulletin de la société chimique de Paris*, **39**, 258 and 263.

§ Presidential address to the chemical section of the British Association for the Advancement of Science, Birmingham Meeting, 1886.

|| *Nature*, **31**, 42—and in a separately published memoir, printed at San Francisco in 1888.

tional *molecules* escape detection; as, for instance, if copper were to be converted into cupric oxide, and for a thousand molecules of the latter a single molecule of cuprous oxide were to be formed, and the fact were for some reason to be overlooked.

Secondly,—Assuming that the atomic weights of the various elements are severally fixed and immutable, are they represented by numbers which are commensurable? Or, putting the question in the more limited form in which it is commonly referred to, are the atomic weights of all the other elements integer multiples of that of hydrogen?

An affirmative answer to this second form of the question constitutes the much discussed "hypothesis of Prout." Of this the original history repays examination, as there are several points in regard to it which do not seem to be generally known. Two years before the appearance of Prout's first paper, Dr. Thos. Thomson pointed out* multiple relations between the atomic weights of several other elements and that of *oxygen*, which he represented by unity, using the following language,—"2. There are eight atoms of simple bodies whose weights are denoted by whole numbers; namely

1.—Oxygen	1
2.—Sulphur	2
3.—Potassium	5
4.—Arsenic	6
5.—Copper	8
6.—Tungsten	8
7.—Uranium	12
8.—Mercury	25

3. An atom of phosphorus is ten times as heavy as an atom of hydrogen. None of the other atoms appear to be multiples of 0·132; so that if we pitch upon hydrogen for our unit, the weights of all the atoms will be fractional quantities, except that of phosphorus alone."

In 1815 there appeared in Dr. Thomson's Annals of Philosophy† an anonymous article, entitled "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms." The article is devoted to a comparison between the volumetric relations of substances in the gaseous state, recently studied with such admirable results by Gay Lussac, and the combining proportions by weight of the same substances. Toward the end of the paper occurs the following passage,—"Table II. This table exhibits many striking instances of the near coincidence of theory and experiment"

* "On the Daltonian Theory of Definite Proportions in Chemical Combinations,"—Annals of Philosophy, **2** (1813), 114.

† Annals of Philosophy, **6** (July to December, 1815), 321.

(*i.e.*, agreement between the weights of the atoms—or, as we should now say, the molecules—of substances as calculated from their density in the gaseous state, and as determined by chemical experiment).—"Table III. This table likewise exhibits some striking examples of the coincidence above noted. Indeed, I had often observed the near approach to round numbers of many of the weights of the atoms, before I was led to investigate the subject. Dr. Thomson appears also to have made the same remark." In the next volume of the Annals of Philosophy, for the first half of 1816, in the "Account of the Improvements in Physical Science during the year 1815, by Thomas Thomson, M.D., F.R.S.," this language was used,*—"A very important paper was published in a late number of the Annals of Philosophy on this subject" (the general principles of the atomic theory). "Though the paper in question is anonymous, several circumstances enable me to fix with considerable certainty on the author; but, as he chooses to remain for the present concealed, I do not consider myself as at liberty to mention his name. The title of the paper is on the Relation between the Specific Gravities of Bodies in their Gaseous State, and the Weight of their Atoms (Annals of Philosophy, **6**, 321). By pointing out this relation he shows that the two modes of viewing the atomic theory come in fact to the same thing." This last sentence correctly states the essential character of Prout's paper; it really relates to what we now call the application of gaseous density (in connection with the law of Avogadro) to the determination of molecular (then called atomic) weight. The remarks as to the multiple relations of other atomic weights to that of hydrogen are incidental only. In the same volume there appeared another anonymous article,† "Correction of a Mistake in the Essay on the relation between the Specific Gravities of bodies in their Gaseous State and the Weights of their Atoms," in which there occurs this paragraph,—"If the views we have ventured to advance be correct, we may almost consider the *πρώτη ὕλη* ‡ of the ancients to be realised in hydrogen; an opinion, by the by, not altogether new. If we actually consider this to be the case, and further consider the specific gravities of bodies in their gaseous state to represent the number of volumes condensed into one; or, in other words, the number of the absolute weight of a single volume of the first matter, *πρώτη ὕλη*, which they contain, which is extremely probable, multiples in weight must always indicate multiples in

* Annals of Philosophy, **7** (Jan. to June, 1816), 17.

† Annals of Philosophy, **7**, 111.

‡ The invention of the name "protyle" has been attributed of late years to Crookes in his address of 1886. This passage shows that Prout used it in 1816, referring to it as a term of ancient philosophy.

volume, and *vice versâ;* and the specific gravities, or absolute weights of all bodies in a gaseous state, must be multiples of the specific gravity or absolute weight of the first matter, *πρώτη ὕλη* because all bodies in a gaseous state which unite with one another unite with reference to their volume." Further on in the same volume may be found* "Some Observations on the Relations between the Specific Gravity of Gaseous Bodies and the Weights of their Atoms. By Thomas Thomson," including this passage,—"Dr. Prout, in a very valuable paper published in the sixth volume of the Annals, has endeavoured to show that the specific gravity of any body" (in the gaseous state is, of course, meant) "may be obtained by multiplying the weight of its atom by half the specific gravity of oxygen gas. This is the same thing as to say that the weight of an atom of every body is always double its specific gravity in the state of gas." Here the name of Prout is first disclosed as that of the author of the anonymous papers. The truth seems to be, that an originally incidental remark of Prout arrested the attention of Thomson, and he and Prout, charmed by the extreme simplicity of the volume relations of substances in the gaseous state (as demonstrated by Gay Lussac) —relations really dependent on the *numbers* of molecules concerned in reactions—thought that they had discovered a like simplicity in the relations between the *weights* of reacting molecules (or atoms, these two being then confounded with each other). For some time such multiple relations continued to be referred to as existing in regard to oxygen as well as hydrogen. The rough approximations to the atomic weights of the elements which alone were available at this time, and for several years later, lent apparent support to the idea of simple multiple relations between them. Thomson, as we have seen, was much influenced by this idea in the adoption of what he supposed to be the true numbers. Berzelius, with his far better analytical results, seemed to disprove the validity of such assumptions. When Dumas undertook to re-examine the combining proportions of carbon and of hydrogen with oxygen, and obtained results which made the atomic weights of carbon and oxygen almost exact integer multiples of that of hydrogen, he seems to have become strongly prepossessed in favour of the hypothesis of Prout, and made his long series of atomic weight determinations with the expectation of finding confirmation for it. In the case of chlorine it had become apparent that, with hydrogen as unity, an integer value was not admissible, but Marignac suggested that the true value was nearly *midway* between the two integers, 35 and 36, and that Prout's idea might still prove to be well founded if the multiple relation were referred to *half* the atomic weight of hydrogen. Later on Dumas

* Annals of Philosophy, 7, 343.

proposed even a further reduction of the unit of multiples, namely to *one-fourth* the weight of an atom of hydrogen.* This proposition has never met with general favour, it being manifest that some evidence should be adduced, other than the mere exigency of the hypothesis, in favour of the divisibility of the hydrogen atom, and that each reduction in the magnitude of the unit adopted increases the likelihood of a number of atomic weights falling pretty near to multiples of such a unit. A widely spread feeling however remained that, as increasing accuracy of analysis should gradually clear away experimental errors, and furnish more exact values for the atomic weights, they would be found to accord with Prout's hypothesis or with some modification of it. How much under the influence of this feeling Stas began his independent researches, has been recorded in his own often-quoted words,†—"" *Je le dis hautement, lorsque j'ai entrepris mes recherches, j'avais une confiance presque absolue dans l'exactitude du principe de Prout.*"

Thirdly,—If we assume the atomic weights of the elements to have constant values, and to be represented by commensurable numbers, does not this indicate that all or most of the elements are in reality compound forms of matter, that those with higher atomic weights are built up out of those with lower, that there are no differences in kind among all known substances save such as grow out of greater or less complexity of composition, and that we are as much called upon to believe in the unity and unlimited interconvertibility of matter as in the unity and interconvertibility of energy? This question, suggested to Prout by his belief in multiple relations among the atomic weights, as his words, already quoted, in regard to the *πρώτη ὑλη* indicate, has time and again been referred to, and its far reaching importance recognized, by later chemists. In recent

* This idea of the atomic weights of the elements being multiples of a smaller unit than the atomic weight of hydrogen is commonly attributed to Marignac and Dumas, but it was suggested at a much earlier day by Prout himself. In the notes at the end of "An Introduction to the Atomic Theory," by Dr. Chas. Daubeny of Oxford, of which the first edition was published in 1831, and the second in 1850, a letter to the author from Prout is published (p. 471 in the 2nd edition), containing the following passage,—"The original opinion to which I was led by the observation of others, and innumerable experiments (never published) of my own, was, that the combining or atomic weights of bodies bear certain simple relations to one another, frequently by multiple, and consequently that many of them must necessarily be multiples of some one unit; but as the atom of hydrogen, the lowest body known, is frequently subdivided when in combination with oxygen, &c., there seems to be no reason why bodies still lower in the scale than hydrogen (similarly however related to one another, as well as to those above hydrogen) may not exist, of which other bodies may be multiples, without being actually multiples of the intermediate hydrogen."

† *Bulletin de l'Académie Royale de Belgique*, 1860, 211.

years it has been discussed at length by Crookes in his address to the Chemical Section of the British Association in 1886, and by Mendelejeff in his Faraday lecture before the Chemical Society in 1889. Stas saw clearly the supreme interest attaching to this idea. He said in 1860,*—"*Au point de vue de la philosophie naturelle, la portée de l'idée de Prout est immense. Les éléments des corps composés que nous considérons comme des corps simples en égard à leur immutabilité absolue pour nous, ne seraient eux-mêmes que des corps composés. Ces éléments, dont la découverte fait la gloire de Lavoisier et a immortalisé son nom, peuvent être considérés ainsi comme dérivant de la condensation d'une matière unique: nous sommes naturellement conduits à l'unité de la matière, quoi qu'en réalité nous constations sa pluralité, sa multiplicité.*"

Fourthly,—Do experiments with substances raised to extremely high temperatures justify the belief that, not only admittedly compound bodies, but also the elements themselves, may thus be dissociated into simpler forms of matter? Some of the modern researches carried out with the aid of the spectroscope, notably those of Norman Lockyer, had seemed to indicate such dissociation, and the possibility of matter in simpler forms than are known to our terrestrial chemistry existing on a vast scale in the atmosphere of the sun, or of some of the more distant heavenly bodies. Stas devoted 11 years to the experimental examination of this great question, and was led by it further to consider the probable conditions under which the emission of solar light takes place, thus extending his researches from the domain of chemistry into that of physics.

In the course of his work, Stas investigated the methods of analysis to be used with a degree of rigour, and discovered and applied refinements upon older modes of experiment with a degree of patience and skill, such as had never before been used in chemical investigation.

He sought out simple and well defined reactions, and examined with the utmost minuteness the conditions under which these reactions were complete, or the limits within which they approached completeness. Good examples are afforded by his direct synthesis of silver chloride, passing a current of chlorine gas over metallic silver heated in a tube of Bohemian glass, in which experiment he detected that the glass was slightly acted on by the fused chloride of silver, traces of an alkaline chloride being formed and carried away with the stream of chlorine—by his discovery that on precipitating a soluble salt of silver with an alkaline chloride a minute amount of silver chloride remains in solution in the residual liquid, which is rendered faintly turbid by the addition of a trace of either of the original salts, but that this does not occur in cold solutions if an

* *Bulletin de l'Académie Royale de Belgique*, 1860, 209.

alkaline bromide, or hydrobromic acid, be substituted for the precipitating chloride—and by the careful study made of the hygroscopic character of the various materials needing to be weighed. He fully recognized the importance of determining an atomic weight by several independent methods, and of requiring close accordance between the results so obtained before accepting them as satisfactory. He laid especial stress upon checking, whenever possible, the analysis of a compound by its synthesis, and of directly determining in each case the weights of the constituents and of the compound itself, drawing the distinction between *complete* synthesis or analysis, and synthesis or analysis *by difference*.

He employed platinum vessels whenever these could be used, studied carefully the changes to which hard glass and porcelain were found to be liable in use, and had experiments set on foot upon a working scale in a glass factory to ascertain the best composition for glass capable of resisting the action of water and acids, but soft enough to be workable. He satisfied himself that the small but continuous loss of weight undergone by glass vessels when heated directly over a gas or alcohol flame might be prevented by imbedding them in a bath of pure magnesia. He had specially made under his directions numerous glass vessels of shapes and sizes adapted to the requirements of his original methods.

He bestowed the most scrupulous care upon the preparation and purification, often by new processes, of all materials used—and, as a precaution against unknown constant errors from this source, applied different methods to the preparation of the same substance, and used the products separately in atomic weight determinations. Thus, for example, he prepared potassium chloride from the nitrate, the chlorate, the platinichloride, and the acid tartrate—sodium chloride from the clearest rock salt, from the acid carbonate, the sulphate, the nitrate, the platinichloride, and the tartrate—silver iodate from potassium iodate and silver nitrate, from potassium iodate and silver sulphate, from iodic acid and silver sulphate, and from potassium iodate and silver dithionate—ammonium chloride (among other methods) by evolving gaseous ammonia from the action of zinc on an alkaline solution of potassium nitrite, acting on a watery solution of this gas with pure gaseous hydrochloric acid, not quite to saturation, crystallizing, and subliming in a platinum vessel in a stream of pure ammonia gas. He purified iodine, either by dissolving it to saturation in a concentrated aqueous solution of potassium iodide, precipitating with an excess of water rather less than sufficient to throw down the full amount possible, washing, distilling with steam, and drying under a bell-glass beside calcium nitrate (the only salt found not to affect the purity of the iodine), or else by acting with solution

of ammonia on the iodine to be treated, thus forming nitrogen iodide, or diiodamine as he considered it, decomposing the violently explosive product by heating with excess of water to 60° or 65° C., distilling and drying as before. By this latter method he treated in all some ten kilogrammes of iodine, generally in lots of 500 grammes at a time. Out of several processes applied to the preparation of pure silver he seems to have preferred the precipitation of a dilute ammoniacal solution of silver nitrate by a solution of ammonio-cuprous sulphite, exhaustion of the precipitated metal with ammonia, and careful washing—the metal was fused in a crucible of pure lime by the oxyhydrogen flame, and heated to its boiling point until the sodium line could no longer be perceived in the spectrum of the vapour, or actually distilled in vessels of lime—when required in the form of sheets the metal was rolled between two plates of silver, so as to avoid the taking up of iron from the rolls.* Pure water was obtained by distilling three times, passing the steam for the first time through a red hot copper tube containing oxidized copper turnings, or distilling from potassium permanganate, then from a little potassium or sodium acid sulphate to retain ammonia, and finally condensing in a long tube of platinum. Novel means of testing the purity of the specially prepared materials were adopted—such as observation of the perfectly bright and lustrous surface, free from stain, of pure silver in fusion, and of the absence of colour in the vapour of the metal when boiling before the oxyhydrogen flame.

The balances used were of excellent construction, and unusually satisfactory both as to sensitiveness and steadiness. A set of weights, from 1 kilogramme down, altogether of platinum, compared with the Paris standards, for the Belgian Government, under the direction of Arago, and a second set, of which the larger pieces were of brass, compared with the former by Stas himself, served for the weighings required—Stas appears to have been the first chemist to apply *in full* to his weighings the proper correction for buoyancy in air. In some cases the substances to be weighed were actually enclosed in exhausted vessels, counterpoised by others of like bulk and character of surface, but in all cases the results were reduced to their equivalent values *in vacuo*.

The practical details of manipulation were worked out with the greatest pains and ingenuity. Liquids were evaporated in closed vessels, avoiding transference and the derivation of impurities from

* When Dumas announced, in 1878, that silver fused and solidified in the air retains occluded oxygen, Stas bestowed much pains upon the examination in this respect of the silver he had used in his researches, and satisfied himself that no oxygen had been retained by it, at any rate in quantity capable of affecting perceptibly his results.

the air, it having been found that evaporation in free air always left a slight residue of organic matter, and in the case of acids sometimes traces of iron, from atmospheric dust. Solution of silver in nitric acid was effected in strong glass vessels, closed by ground stoppers, to avoid any loss of the solution in the form of fine spray carried off by the escaping gas. Exact measurement of liquids was accomplished by means of well devised and carefully calibrated pipettes, surrounded by water for the maintenance of uniform temperature In precipitations of chloride or bromide of silver the end of the reaction was observed in a chamber the inner surface of which was painted with lamp black, and in which the only light was derived from a gas jet, and was transmitted through a screen of yellow glass or through a glass globe containing a solution of potassium chromate.

Unusually large quantities of interacting substances were used, as, for example, 77—405 grammes of silver converted into nitrate and weighed as such, 60—250 grammes of silver converted into sulphide, 139—259 grammes of silver chlorate converted into chloride, &c. In analyses or syntheses involving precipitation, extensive use was made of the valuable method, first suggested by Pelouze, of taking a small excess of one of the two interacting substances, and, after complete action, and subsidence of the precipitate, determining the exact amount of the substance used in excess remaining in the solution. Stas appreciated highly the neatness and precision of this process. In a letter to the writer of this paper, dated January 27th, 1887, he spoke thus of it,—"*Je me permets de vous recommander l'emploi de l'acide bromhydrique pour la précipitation de l'argent resté dans un liquide après une double décomposition opérée à l'aide d'un* CHLORURE *et d'un sel d'argent. On réussit à condition que l'eau mère renferme un excès d'argent dont le poids est le triple du métal qui peut rester en solution à l'état de chlorure d'argent. En opérant dans un flacon bouché dont on a déterminé avec soin la capacité, en prélevant un volume connu de l'eau mère dont le volume total est égal a la capacité du flacon, moins celui du chlorure d'argent, on peut aisément déterminer l'argent contenu dans la partie prélevée en recevant celle-ci dans un flacon ou on a introduit du bromure d'argent bien lavé. Je compte recourir à cette méthode pour contrôler les recherchés que je vais entreprendre sur le chlorure de potassium. Par mes travaux antérieurs j'ai trouvé que le chlorure de potassium et l'argent employés pour une double décomposition, pris dans le rapport de 74·5 à 108, laissent par 10 grs. de chlorure de 25·55 mgr. à 28·66 mgr. d'argent libre. Le moyen indiqué ci-dessus appliqué à du chlorure de potassium pur permet de contrôler ces résultats à 0·05 mgr. près.*"

Originally all the determinations of atomic weights were referred to oxygen = 8—or, later, to oxygen = 16—but were afterwards calcu-

lated on the basis of hydrogen = 1. Stas' views as to this question of standard are given in the following passage from his great paper of 1865;* in this the words emphasized are so used by himself,—"*J'ai dit expressément que toutes ces valeurs sont déterminées en fonction de l'oxygène pris* HYPOTHÉTIQUEMENT *égal à* 16. *Si on les rapporte à l'hydrogène pris pour unité, on doit nécessairement les corriger, du fait que la différence qui existe entre le poids atomique de l'oxygène déduit de l'expérience et le poids atomique admis par hypothèse. Or, le rapport de l'hydrogène à l'oxygène n'est pas connu avec certitude. De l'ensemble de tous les travaux exécutés sur la composition de l'eau, sur la pesanteur spécifique de l'hydrogène et de l'oxygène, sur le rapport proportionnel entre le chlorure d'ammonium et l'argent, je suis* PORTÉ À CROIRE *que l'hydrogène étant* 1, *le poids atomique de l'oxygène ne peut guère dépasser* 15·96."

To what results did Stas' elaborate researches lead? They may be briefly summed up as follows—

1st—He determined the following atomic weights †—

	Oxygen (assumed) = 16.	Hydrogen = 1.
Oxygen	16·	15·960
Silver	107·930	107·660
Nitrogen	14·055	14·019
Sulphur	32·0703	31·9901
Chlorine	35·457	35·368
Bromine	79·952	79·750
Iodine	126·850	126·533
Potassium	39·1425	39·044
Sodium	23·0455	22·988
Lithium	7·022	7·004
Lead	206·913	206·396
Carbon	11·999	11·969

with a degree of concordance between his numerous individual results so great that the extreme variation for each element is only represented by ·005 to ·01.

2nd—He proved that in the case of ammonium chloride at least, changes of temperature or pressure within wide limits are without any perceptible influence upon the proportions in which the con-

* *Mémoires de l'Académie Royale de Belgique*, **35** (1865), 24.

† The number for sulphur has been corrected in accordance with Stas' revision of that for silver. The number for lead is the mean between the results obtained from the sulphate and from the nitrate. The number for carbon is the mean between the results obtained (with Dumas) from the combustion of elementary carbon and (by Stas alone, in 1849) from the combustion of carbon monoxide. The recalculation by Van der Plaats of the atomic weights in the table from Stas' experimental data brings out some very small differences. *Annales de Chimie et de Physique* [6], **7** (1886), 499, but the figures of the table are those of Stas himself.

stituents are combined, and that in such salts as the iodate and bromate of silver the halogens are united to silver in sensibly the very same proportions as in the iodide and bromide. From these, and all other facts of his experiments having the same bearing, he came to the conclusion that the atomic weights of the elements, determined by independent methods, have really constant values in all the compounds in which they occur, no matter how they are associated, or under what physical conditions combination may take place.

3rd—He satisfied himself that the atomic weights of the elements which he determined with such precision are not commensurable, that they cannot with truth be represented by integer multiples of the atomic weight of hydrogen, or of the half, or the fourth of this unit, and that, while his original prepossession was (as has been quoted in his own words) strongly in favour of Prout's hypothesis, he found it to be clearly contradicted by his experimental results. He pointed out that the mean value for an atomic weight derived from these results differed from the value required by Prout's hypothesis to an extent twice to fourteen times as great as the extreme difference between the maximum and minimum individual results from which the mean was calculated. Again to quote his own words,—"*Je termine donc en disant : aussi longtemps que, pour l'établissement des lois qui régissent la matière on veut s'en tenir à l'expérience, on doit considérer la loi de Prout comme une pure illusion.*" "*La simplicité de rapport de poids que présuppose l'hypothèse de Prout entre les masses qui interviennent dans l'action chimique, ne s'observe donc point dans l'expérience ; elle n'existe point dans la réalité des choses.*" The great majority of chemists at the present day are probably agreed in believing that the hypothesis of Prout has by Stas been shown to be untenable. But the fact that so many well determined atomic weights, referred to hydrogen as unity, present numbers *nearly approaching* integers, is very striking, and calls for further investigation. The writer of this paper is in a position to quote Stas himself as admitting this much. Having enjoyed the pleasure of a conversation of considerable length with the eminent Belgian chemist at his house in Brussels in the summer of 1887, and having urged upon him the improbability of this near approach to integer values for so many atomic weights being due to chance alone, the writer was answered by the remark, "*Il faut croire qu'il y a quelque chose la-dessous.*"

4th—He concluded, both from the evidence in disproof of Prout's hypothesis, and from his long series of spectroscopic experiments at the highest attainable temperatures, using materials purified with the refinement of methods which he had devised, that no facts now known to us justify a belief in the dissociability of the atoms of the chemical

elements, their interconvertibility, or their production by aggregation from hydrogen or any other yet simpler form of matter. By us, in our present state of knowledge, they must be regarded as primordially and inalterably distinct substances,—"*individualités à part*," as Stas himself called them. "The unity of matter" must be viewed as an attractive speculation unsupported by proof.

The titles of Stas' memoirs on this subject, as they originally appeared, are given in the following—

List of Papers by Stas on Atomic Weight Determinations.

Recherches sur le véritable poid atomique du carbone (with Dumas) —*Comptes rendus*, **11**, (1840), 991—*Annales de Chimie et de Physique*, **1** (1841), 5.

Recherches sur le véritable poids atomique du carbone (combustion of carbon mon-oxide)—*Bulletin de l'Académie Royale de Belgique*, **16** (1849), 9.

Recherches sur les rapports réciproques des poids atomiques—Bulletin de l'Académie Royale de Belgique, **10** (1860), 208.

Nouvelles recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels. (Présenté à l'Académie, le 14 Janvier, 1865)—*Mémoires de l'Académie Royale de Belgique*, **35** (1865), 3.

Sur une modification de la méthode d'essai des matières d'argent par voie humide—Comptes rendus, **67** (1868), 1107.

Recherches de statique chimique. Des phénomènes qui se passent dans la précipitation mutuelle des solutions diluées des sels d'argent par les acides chlorhydrique, bromhydrique, iodhydrique, et les chlorures, bromures et iodures—Comptes rendus, **73** (1871), 998.

Recherches de statique chimique au sujet du chlorure et du bromure d'argent—Annales de Chimie et de Physique [4], **25** (1872), 22.

Recherches de statique chimique au sujet du chlorure et du bromure d'argent, 2e partie—Annales de Chimie et de Physique [5], **3** (1874), 145.

De la détermination du rapport proportionnel entre l'argent, les chlorures et les bromures ("*Mémoire présenté à la classe des sciences dans la séance du 5 Août*, 1876")—*Mémoires de l'Académie Royale de Belgique*, **43** (1882), 3.

As partially related to his work on atomic weights, there may also be noted,

Discours de la nature de la lumière solaire—Mémoires de l'Académie Royale de Belgique, **49** (1891).

From 1860 to 1881 much work was done by other chemists in reference to atomic weights, and the following names are quoted.

Atomic Weight Determinations from 1860 *to the end of* 1881.

Within this period appeared papers by the following chemists.

R. W. Bunsen	1861–70	C. Czudnowicz	1860–63
F. Kessler	1861	J. Schiel	1861
C. Scheibler	1861	M. Siewert	1861
K. Diehl	1862	L. Troost	1862
J. Piccard	1862	S. W. Johnson and O. D. Allen	1863
W. J. Russell	1863–69	E. Millon and Comaille	1863
A. Lamy	1863	J. J. Chydenius	1863
M. Delafontaine	1864–66	F. Reich and T. Richter	1864
C. W. Blomstrand	1864	H. Werther	1864
W. Crookes	1864–73	O. Popp	1864
J. Persoz	1864	R. Hermann	1864
C. Winkler	1865-67	M. Hebberling	1865
C. Marignac	1865–66	J. F. Bahr and R. W. Bunsen	1866
E. v. Sommaruga	1867	E. Zettnow	1867
G. Klatzo	1868	Isnard	1868
C. Wolf	1868	H. Debray	1868
H. E. Roscoe	1868–81	H. Zschiesche	1868–69
P. Weselsky	1869	C. E. Claus	1869
C. Erk	1870	C. H. Wing	1870
J. Thomsen	1870	R. H. Lee	1871
H. Buehrig	1873	W. Hampe	1873
P. T. Cleve and O. M. Hoeglund	1873	P. Liechti and B. Kempe	1873
L. Meyer	1874	P. T. Cleve	1874
C. Rammelsberg	1874	H. F. Weber	1875
R. Godeffroy	1876–77	W. F. Hillebrand	1876
O. Pettersson and G. Ekman	1876	J. Emerson Reynolds	1877
J. P. Cooke	1877–80	K. Seubert	1878–80
Lecoq de Boisbaudran	1878	M. Berthelot	1878
A. Terrill	1879	W. L. Wills	1879
J. S. Humpidge and W. Burney	1879	L. F. Nilson	1880
J. W. Mallet	1880	L. F. Nilson and O. Pettersson	1880
R. Schneider	1881	F. Pfeifer	1881
J. Dewar and A. Scott	1881	O. W. Huntington	1881

So far, only names and dates have been given, in view of the fact that up to 1882 all the work previously done on atomic weight determinations has already been thoroughly well collected, reported on, and discussed in certain works devoted to this subject in general form. Anyone who may have need of detailed information can find it, with copious references to original authorities, in the following

Collective Discussion of Atomic Weight Determinations.

W. A. J. Van Geuns—*Proeve eener Geschiedenis van de Æquivalentgetallen der Scheikundige Grondstoffen en van hare Soortelijke Gewigten in Gasvorm, voornamelijk in Betrekking tot de vier Grondstoffen der Bewerktuigde Natuur.* Amsterdam, 1853.

E. Mulder—*Historisch-Kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van* 13 *Eenvoudige Ligchamen.* Utrecht, 1853.

L. Mulder—*Historisch-Kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van* 24 *Metalen.* Utrecht, 1853.

A. C. Oudemans, Jr.—*Historisch-Kritisch Overzigt van de Bepaling der Æquivalent-Gewigten van Twee en Twintig Metalen.* Leiden, 1853.

G. F. Becker—The Constants of Nature, Part IV; Atomic Weight determinations, a digest of the investigations published since 1814. Smithsonian Miscellaneous Collections. Washington, D.C., 1880.

F. W. Clarke—The Constants of Nature, Part V; A recalculation of the Atomic Weights. Smithsonian Miscellaneous Collections. Washington, D.C., 1882.

L. Meyer u. K. Seubert—*Die Atomgewichte der Elemente aus den Originalzahlen neu berechnet.* Leipzig, 1883, to which may be added, though of later date,

J. Sebelien—*Beiträge zur Geschichte der Atomgewichte; eine von der Universität zu Kopenhagen gekrönte Preisschrift.* Braunschweig, 1884.

J. D. Van der Plaats—*Essai de calcul des poids atomiques de M. Stas—Annales de Chimie et de Physique* [6], **7** (1886), 499.

In order to carry on the record of the literature of atomic weight determinations since the appearance of the important works of Becker, Clarke, and Meyer and Seubert, the following list of references has been prepared, quoting in each case the original paper, as far as known.

Papers on Atomic Weight Determinations since the Beginning of 1882. (*Including some Papers of a Physical Character bearing on Atomic Weights.*)

1882.

Thorium	L. F. Nilson	*Berichte d. deutsch. chem. Gesellschaft*, **15**, 2527.
Lanthanum..	B. Brauner	Jour. Chem. Soc., Feb., 1882, 75.
Didymium ..	B. Brauner	Jour. Chem. Soc., Feb., 1882, 75.—*Wien Akad. Ber.*, 86, June, 1882.
Rubidium ..	Ch. F. Heycock.....	*Bribl. z. d. Ann. d. Phys. u. Chemie*, **6**, 838.—Nature, **26**, 444.
Yttrium ..	P. T. Cleve	*Comptes rendus*, **95**, 1225.

1883.

Didymium ..	P. T. Cleve	*Öfversigt af. K. Sv. Vetensk. Akad. Förhandl.*, 1883, No. **2**, 23.
Samarium ..	P. T. Cleve	*Öfversigt af. K. Sv. Vetensk. Akad. Förhandl.*, 1883, No. **7**, 17.

Bismuth .... Manganese .. Zinc ..... Magnesium..	C. Marignac	*Archives des sciences phys. et nat.* [3], **10**, 5 and 193.
Copper .... Zinc ..... Nickel.....	H. Baubigny	*Comptes rendus*, **97**, 854, 906 and 951.
Beryllium ..	T. S. Humpidge.....	Proc. Roy. Soc., **35**, 137.
Antimony ..	J. Bongartz	*Berichte d. deutsch. chem. Gesellschaft*, **16**, 1942.
Aluminum ..	H. Baubigny	*Comptes rendus*, **97**, 1369.
Titanium ..	T. E. Thorpe	Proc. Roy. Soc., Nov. 22, 1883—Chem, News, **48**, 251.
Tellurium ..	B. Brauner	Prot. i. J. d. russ. phys. chem. Gesellsch., 1883 (1), 433—*Berichte d. deutsch. chem. Gesellschaft*, **16**, 3055.
Didymium ..	B. Brauner	Jour. Chem. Soc., June, 1883.
Molybdenum	Otto von der Pfordten	Inaugural dissertation, Giessen, 1883.
1884.		
Cerium	H. Robinson	Chem. News, **50**, 251.
Platinum ..	W. Halberstadt.....	*Berichte d. deutsch. chem. Gesellschaft*, **17**, 2962.
Chromium ..	H. Baubigny	*Comptes rendus*, **98**, 143.
1885.		
Carbon .... Phosphorus.. Tin ..... Zinc.....	J. D. van der Plaats ..	*Comptes rendus*, **100**, 52.
Beryllium ..	T. S. Humpidge	Proc. Roy. Soc., Mar. 5, 1885.
Titanium ..	T. E. Thorpe	Jour. Chem. Soc., **47**, 108.
Cerium	B. Brauner.....	Jour. Chem. Soc., **47**, 879—*Sitzungsberichte d. kaiserl. Akad. d. Wissenschaften in Wien*, II Abth., **92**, 814.
Oxygen	Agamennone	*Atti dei Lincei*, 1885.
1886.		
Uranium ..	C. Zimmermann	*Annalen d. Chemie*, **232**, 273.
Germanium	C. Winkler	*Journ. für prakt. Chemie* [N.F.], **34**, 202.
Germanium	Lecoq de Boisbaudran	*Comptes rendus*, **103**, 452.
Antimony ..	A. Popper	*Annalen d. Chemie*, **233**, 153.
Cerium	H. Robinson	Chem. News, **54**, 229.
Nickel .... Cobalt	C. Zimmermann....	*Annalen d. Chemie*, **232**, 324.
Tungsten ..	J. Waddell.....	Amer. Chem. Journal, **8**, 280.
Gold	G. Krüss.....	*Annalen d. Chemie*, **238**, 241—*Berichte d. deutsch. chem. Gesellschaft*, **20**, 205 and 2355—**21**, 126.
1887.		
Fluorine....	O. T. Christensen	*Journ. für prakt. Chemie* [N.F.], **35**, 547.
Oxygen	E. H. Keiser	*Berichte d. deutsch. chem. Gesellschaft*, **20**, 2323.
Silver ..... Copper	W. N. Shaw	Phil. Mag. [5], **23**, 138.

Thorium....	G. Krüss and L. F. Nilson.	*Berichte d. deutsch. chem. Gesellschaft*, **20**, 1665.
Oxygen	J. P. Cooke and T. W. Richards.	Proc. Amer. Acad. Arts and Sci., **23**, 149—Amer. Chem. Jour., **10**, 81.
Gold	T. E. Thorpe and P. A. Laurie.	Jour. Chem. Soc., **51**, 565.
Silicon.....	T. E. Thorpe and J. W. Young.	Jour. Chem. Soc., **51**, 576.
Copper	T. W. Richards	Proc. Amer. Acad. Arts and Sci., **22**, 342.
Zinc	H. C. Reynolds and W. Ramsay.	Jour. Chem. Soc., **51**, 854.
Oxygen	A. Scott	Proc. Roy. Soc., **42**, 396—Proc. Brit. Assoc., 1887, 668.
1888.		
Osmium	K. Seubert	*Berichte d. deutsch. chem. Gesellschaft*, **21**, 1839—*Annalen d. Chemie*, **261**, 257.
Oxygen	J. P. Cooke and T. W. Richards.	Proc. Amer. Acad. Arts and Sci., **23**, 182.
Zinc	H. N. Morse and W. M. Burton.	Amer. Chem. Journal, **10**, 311.
Platinum .. Rubidium ..	W. Dittmar and J. McArthur.	Trans. Roy. Soc. Edinburgh, **33**, II, 561.
Copper	T. W. Richards	Proc. Amer. Acad. Arts and Sci., **23**, 177.
Tin	J. Bongartz and A. Classen.	*Berichte d. deutsch. chem. Gesellschaft*, **21**, 2900.
Oxygen	Lord Rayleigh	Proc. Roy. Soc., **43**, 356.
Oxygen	A. Scott	Proc. Brit. Assoc., 1888, 631—Nature, **37**, 439.
Oxygen .... Nitrogen....	J. M. Crafts	*Comptes rendus*, **106**, 1662.
1889.		
Zinc	J. H. Gladstone and W. Hibbert.	Jour. Chem. Soc., **56**, 443.
Palladium ..	E. H. Keiser	Amer. Chem. Journal, **11**, 398—Jour. Franklin Institute, 1889.
Chromium ..	S. G. Rawson.....	Jour. Chem. Soc., **55**, 213.
Gold	J. W. Mallet	Phil. Trans., 1889, A, 395.
Tellurium ..	B. Brauner	Jour. Chem. Soc., **54**, 382—*Sitzungsberichte d. Kaiserl. Akad. d. Wissenschaften in Wien*, **98**, Abth. II b. 456.
Zirconium ..	C. H. Bailey	Proc. Roy. Soc., May 9, 1889—Chem. News, **60**, 6.
Oxygen	W. A. Noyes	Amer. Chem. Journal, **11**, 155.
Beryllium ..	G. Krüss and H. Moraht.	*Annalen d. Chemie*, **262**, 38.
Ruthenium..	A. Joly	*Comptes rendus*, **108**, 946.
Oxygen	J. P. Cooke	Proc. Amer. Acad. Arts and Sci., **24** (1889)—Amer. Chem. Journal, **11**, 509.
Oxygen	Lord Rayleigh	Proc. Roy. Soc., **45**, 425.
1890.		
Bismuth	A. Classen	*Berichte d. deutsch. chem. Gesellschaft.*

Iridium	A. Joly	*Comptes rendus*, **110**, 1131.
Magnesium..	W. M. Burton and L. D. Vorce.	Amer. Chem. Journal, **12**, 219—Chem. News, **62**, 267.
Fluorine....	H. Moissan.....	*Comptes rendus*, **111**, 570.
Cadmium ..	E. A. Partridge	Amer. Jour. Sci. [3], **40**, 377.
Chromium ..	C. Meineke	*Annalen d. Chemie*, **261**, 339.
Rhodium ..	K. Seubert and K. Kobbé.	*Annalen d. Chemie*, **260**, 314.
Oxygen	W. A. Noyes	Amer. Chem. Jour., **12**, 441.
Oxygen	E. W. Morley.....	Amer. Chem. Jour., **12**, 460.
Copper .... 1891.	T. W. Richards	Proc. Amer. Acad. Arts and Sci., **25**, 195.
Oxygen	W. A. Noyes	Amer. Chem. Jour., **13**, 354.
Copper	T. W. Richards	Proc. Amer. Acad. Arts and Sci., **26**, 240.
Oxygen .... 1892 (to Nov. 1st).	E. W. Morley	Amer. Jour. Sci. [3], **41**, 220 and 276.
Cadmium ..	H. N. Morse and H. C. Jones.	Amer. Chem. Journal, **14**, 261.
Masrium (?)	H. D. Richmond and Hussein Off.	Jour. Chem. Soc., **61**, 491.
Nickel..... Cobalt.....	P. Schützenberger....	*Comptes rendus*, **114**, 1149.
Cadmium ..	W. S. Lorimer and E. F. Smith.	*Zeitschrift für anorganische Chemie* (G. Krüss), **1** (1892), **5**, 364.
Oxygen	A. Leduc	*Comptes rendus*, **115**, 41.
Oxygen	Lord Rayleigh	Proc. Roy. Soc., Feb. 18, 1892.
Boron	J. L. H. Abrahall	Jour. Chem. Soc., **62**, 650.
Palladium ..	G. H. Bailey and Th. Lamb.	Jour. Chem. Soc., **62**, 745.
Boron	W. Ramsay and Emily Aston.	(Brit. Assoc. Adv. Sci., Edinburgh)—Chem. News, **66**, 92, Jour. Chem. Soc.
Palladium ...	H. F. Keller and E. F. Smith.	Amer. Chem. Jour., **14**, 423.

Present prospect for future work in regard to Atomic Weights and their Determination, and objects of which the attainment seems desirable in respect to the Determination of Atomic Weights.

The scientific outlook in this direction, viewed from the standpoint of our knowledge at present, may be briefly noticed as respects the objects to be aimed at and the methods to be pursued.

1. Though the skill and care bestowed by Stas upon his experiments may well seem to render any repetition of them by others needless, he himself, at the end of his great paper of 1865, expressed the earnest wish that some other chemist, of sufficiently well established scientific authority, would take the trouble to check by repetition some one at least of his fundamental results,* and in closing his paper of 1881† he repeats and emphasizes this wish. It is much to

* *Mémoires de l'Académie Royale de Belgique*, **35**, 305.

† Ditto, **42**, 65.

be desired that his appeal shall not remain without response. There is little doubt that a repetition of his work would but serve to enhance our confidence in its accuracy.

2. It is eminently desirable that the work which Stas did for a few of the elements be extended to the entire list of those known. Viewed in a purely scientific light there should be no distinction made between *common* and *rare* elements; all are equally entitled to careful study. Furthermore, on account of the mutual character of combining proportions, the list of elements should be treated as a consistent whole; the greater the number of well determined atomic weights we have, the more easily can others be obtained and checked. A less common element may present peculiarities of behaviour fitting it better than others more abundant for comparison with new material for experiment, as is illustrated by the superior advantages of the bromides over the chlorides for accurate determination of the halogen as compared with that with which it is combined.

3. Certain of the elements particularly call for a more searching and exact investigation of their atomic weights. A prominent example is presented by tellurium; Brauner's work suggests most attractively a possible explanation of the want of harmony between the undoubted place of this element in the Mendelejeff classification and its atomic weight as determined by experiment, but we have no right to assume the presence as an impurity of an as yet unknown substance of higher atomic weight without having any direct proof that such a substance exists. As another instance, which does not seem to have been heretofore noticed—out of the numerous researches on the atomic weights of nickel and cobalt some have given practically identical results for the two metals, while the general tendency of the remainder has been to assign to cobalt a rather higher atomic weight than to nickel; yet on comparing the properties of the three sets of tetrad and octad metals which compose Mendelejeff's eighth group, viz., Fe, Co, Ni—Ru, Rh, Pd—Os, Ir, Pt, cobalt plainly occupies the intermediate place between iron and nickel, and should, therefore, be expected to possess an intermediate atomic weight, as has been shown by recent investigation to be true of rhodium and iridium in the two sets of platinum metals. Another element of which, on various grounds, it is much to be wished that the atomic weight should undergo a careful revision is mercury, and the writer of this paper has some time ago made a beginning of work in this direction, but the task has already proved itself to be one of much difficulty.

4. There are several atomic weights for which we have numerous and concordant data, but these depend almost entirely upon a single interaction. Thus the value for iron rests practically upon

the conversion of the metal into ferric oxide or the converse. In the same way, numerous experiments to establish the relation between oxygen and hydrogen have been made by the process—rendered classic by Dumas—of passing hydrogen gas over heated cupric oxide. It is desirable that in such cases other and independent methods should be resorted to. Even if the principle adopted remain the same, a change in the nature of the particular substances used would tend to detect possible constant errors; it would be well to repeat the quantitative production of water from hydrogen with the oxides of several other elements than copper, say lead, tin, vanadium and tungsten, severally.

5. It is eminently desirable that an attempt be made to determine directly the ratio between the atomic weight of hydrogen and that of each of the halogens, without in any way bringing in the atomic weight of oxygen. This would undoubtedly be a difficult undertaking, but a successful result would be of great value, both as opening up an easy road by which to connect the atomic weights of many of the electro-positive elements with that of hydrogen, through chlorine, bromine, &c., instead of through oxygen, and as affording an important control upon the value for the last-named element itself. Various methods suggest themselves as possibly available, but they would have to be carefully studied before deciding on their feasibility. Thus hydrogen might be passed over heated chloride or bromide of silver, with an arrangement for collecting (perhaps by solid potash) the hydrogen chloride or bromide formed, weighing the original salt, the collected hydride, and the residual silver.* A serious objection to this arises from the great difference between the weight of the hydrogen and that of the halogen with which it combines. Again, a method might be tried analogous to one used by the writer of this paper in determining the atomic weight of gold, namely, to ascertain the volume of hydrogen liberated by a known weight of zinc from sulphuric acid used in small excess and to compare with this the volume of hydrogen obtained from the same materials in presence of a known weight of silver chloride, the latter completely reduced to metal and weighed, leaving a measurable surplus of free hydrogen, the ratio of silver to chlorine assumed to be already accurately known. Or, conceivably, the direct ratio of chlorine to nitrogen might be determined in NCl_3 (if the absence of hydrogen were fully estab-

* Possibly a synthesis in opposite form might be effected by evolving chlorine from aurous or platinous chloride by heat, passing the gas over spongy palladium charged with hydrogen (removing surplus chlorine afterwards from the residual palladium by ignition in a Sprengel vacuum), collecting the hydrogen chloride formed, and determining in it any free chlorine by Bunsen's iodometric, or some other equivalent, method.

lished), that of chlorine to carbon in CCl_4, of chlorine to phosphorus in PCl_3 or PCl_5, and then the analysis be made of compounds containing these elements *plus* hydrogen, such as NH_4Cl, $C_2H_4Cl_2$, and PH_4Cl; this would enable the difference in weight between hydrogen and chlorine to be diminished, selecting compounds containing several atoms of the former. Or, once more, without getting rid altogether of the influence of the atomic weight of oxygen, but reducing materially this influence, parallel analyses might be made under the same conditions, by the ordinary combustion process, of a hydrocarbon with a considerable and well ascertained number of hydrogen atoms—say, C_7H_{16}—and of a mono-chlor derivative from the same, such as $C_7H_{15}Cl$; this would still further diminish the disproportion between the quantities of hydrogen and chlorine. In the same line of investigation, avoiding the relation to oxygen of the elements concerned, it would be well to determine the ratio of carbon to nitrogen in a metallic cyanide, as for example in the cyanide of silver, and thus connect carbon and nitrogen with hydrogen by the analysis of an alcoholic cyanide or carbamine.

6. The experiments of Stas aiming directly at a settlement of the question whether the atomic weight of an element is really a constant quantity, may be fairly considered to have decided that such absolute constancy of value exists, and this conclusion is on the whole supported by the great mass of accumulated evidence drawn from the researches of others. But we have one group of elements, that of which so-called yttrium is the type, which almost seems to present an exception to the rule. So similar in properties, and so hard to separate, are these substances that, although the rest of our list of elements is clear and in good order, here we find apparently hopeless confusion. No one can say how many of these yttrium metals there are, no two chemists agree fully as to the identity of any one of them in a state of purity, no two sets of experiments give thoroughly constant atomic weights, and, in spite of all the labour bestowed by able chemists of recent years upon the group, it remains the opprobrium of inorganic chemistry. To clear up this anomaly, and to obtain from this group at least some elementary substances of really definite character, and presenting fixed and well determined atomic weights, is one of the problems remaining to be solved. Some, but much less, doubt of the same sort hangs over didymium and its associates, cerium and lanthanum.

7. It would be well to submit to the test of experiment, by means as refined as those employed by Stas, the question of the absolute exactness of the well known "law of multiples"—to ascertain, for instance, whether, for the same quantity of mercury, the quantity of chlorine in corrosive sublimate is precisely twice as great as that in

calomel; whether, for a given amount of copper, cupric oxide contains exactly twice as much oxygen as cuprous oxide, &c. This may seem superfluous, and indeed to assume that the law is not rigidly true is to shake the foundation of the whole of the Daltonian atomic theory. But, remembering what pains Stas was willing to take in order to place the constancy of the atomic weights upon a basis of direct experimental evidence, it may be permissible to suggest this, which is in reality but another form of the same question.

8. In considering the state in which Stas' labours have left the much debated question of the validity of Prout's hypothesis, with its weighty consequences, it may be admitted that in one sense the question—*i.e.*, the question in its original form—has by Stas been settled, and yet it may be considered that this has only led to the substitution of a new question for the former one. If we observe the nearness with which a large proportion of the best determined atomic weights approach to integer multiples of the hydrogen unit, we may imagine two different explanations of the fact, without having recourse to the idea—shown by the calculus of probabilities to be a very improbable one—that this is purely the result of chance. On the one hand, it may be supposed that undiscovered sources of constant errors vitiate the results of our best experiments, and that, if these sources of error could be discovered and eliminated, the numbers representing atomic weights on the scale of the hydrogen unit would turn out to be really integers. This supposition cannot, in the nature of things, be pronounced an impossible one, but it appeals not to what we know, but only to what we may conceivably know in the future and do not know now. It may be reasonably said that probability is against the idea of any future discovery in regard to chlorine, or in regard to the methods by which its atomic weight has been determined, ever making the value for this element agree with an integer multiple of the atomic weight of hydrogen, or of one-half or one fourth of the latter. For several other atomic weights the divergence is much smaller, and might not improbably be removed by the discovery of some as yet unsuspected cause of constant error. On the other hand, it is conceivable, without any assumption of error in the values as we have them for a number of the elements, that some secondary cause may be involved which modifies, or masks the simplicity of, a really underlying relation. If this be admitted, the search for such a secondary cause, to account for the many cases of near approach to integer numbers on the hydrogen scale, is undoubtedly a worthy direction of effort. In any case, one can scarcely look over a list of our best determined atomic weights, and notice the numbers which are being added to this list in the progress of research, without

feeling a strong curiosity on the subject of the close approach of so many of these values to the integer multiples called for by the rejected hypothesis of Prout.

9. Lastly,—out of the numerous attempts in the past to trace numerical relations among the atomic weights of the elements, we have seen emerge a successful and important result. Foreshadowed by the earlier ideas of De Chancourtois and Newlands, Mendelejeff's "periodic law" has manifestly given us a rational classification of the elements, based upon an essential relation between their atomic weights and their other properties. But nearly all that has been written in regard to this relation has so far referred to it in a very general form, involving the use of roughly approximate atomic weights only. Mendelejeff's own tables quote oxygen as represented by 16, chlorine by 35·5, silver by 108, &c. Is it not time that the foundation be laid for a far more minute and critical study of the periodic classification of the elements by securing as far as possible a more exact knowledge of the atomic weights upon which it rests? Stas said, in his memoir of 1865, of Prout's hypothesis,—"*Il me serait par trop aisé de prouver que le chimiste anglais s'est contenté d'*À PEU PRÈS, *autorisés peut-être à son époque.*" May we not say now, in regard to the study of the elements as related to the "periodic law," that the day of "*à peu près*" has gone by? Anomalies in the classification as we now find it in our books, glimpses of more detailed relations than as yet clearly appear, tantalizing suggestiveness in so much of what is already before us, call for more precise determinations of the numbers we would discuss before we allow premature discussion to drift into mere fanciful speculation.

Methods which it is desirable shall be pursued in the Determination of Atomic Weights.

1. *Selection of analytical or synthetical processes.*—Each interaction employed should be as simple and definite as possible, and should admit of the materials used, and the products obtained, being had in forms adapted to accurate weighing. In each case compounds are to be preferred which contain the element of which the atomic weight is to be determined united to as few other elements as possible, and these with already well ascertained atomic weights. The connection of the atomic weight to be determined with the primary unit should be established directly, if possible—otherwise, by as short a chain of intermediate relations as possible. As many different and independent methods as possible should be made use of; if the results of these lead to closely agreeing values for the atomic weight sought, the mean of these may be accepted with confidence; if there be difference amongst

the values obtained from independent sources, a study of these may indicate the direction in which to seek for sources of constant error (*e.g.*—the difference between Stas' results for the atomic weight of nitrogen, as based on the analysis of silver nitrate and ammonium chloride respectively, suggested to him the probable existence of an error in the ratio assumed for oxygen as compared with hydrogen). Agreement between the results of different analyses was first pointed out by Berzelius as the test of accuracy; he applied it, in repetitions of the same process, to detect *casual* errors; in comparisons of the results of different processes it is the ultimate test for *constant* errors. As an extension of the same principle, methods may well be selected which presumably will tend to cause errors, if any, in opposite directions; not with a view to taking the mean of the results, and assuming it to be accurate, but only in order to increase the likelihood of detecting the existence of errors. Whenever possible, the "complete analysis" and "complete synthesis" recommended by Stas should be carried out; this may be rendered more feasible in some cases involving the use of gaseous material by evolving a gas from, or collecting it in, a solid form, as for instance in Keiser's use of spongy palladium charged with hydrogen.

2. *Use of pure materials.*—The researches of Stas illustrate the need for careful and original study of processes by which the substances to be used for an atomic weight determination may be obtained in a state most nearly approaching purity. In establishing the fact of a substance being sensibly pure, recourse may now be had to tests far more delicate than were formerly available, such as spectroscopic behaviour, phosphorescence in exhausted tubes, electric conductivity, and voltaic electro-motive force. Such tests must be applied with due caution, that differences of physical structure be not confounded with those of chemical nature. The most important means, however, of verifying the purity of material, consists in the application of fractional methods of purification, and the subsequent use of separate fractions, particularly the early and late fractions, for experiments from which an atomic weight is to be deduced, only resting satisfied when these different fractions give results in which no constant difference can be detected.

3. *Vigilance in regard to extraneous or accidental causes of error.*—In the determination of an atomic weight the chemist must be on his guard against casual influence upon his experiments of any and all of the surrounding conditions. Among matters of this kind calling for attention may be noted the occlusion of gases, especially by the metals. Dumas' detection of occluded oxygen in silver which had been fused and solidified in the air did not to any important extent affect the results of Stas, but it arrested attention everywhere as an

illustration of a long unsuspected source of error. Beside the long known and important cases of gaseous occlusion by the metals of the platinum group, among facts of this kind recently observed may be mentioned the occlusion of nitrogen by cupric oxide,* of hydrogen by metallic copper,† and of hydrogen by nickel and cobalt‡ (in very unequal quantities by the two metals). The secondary phenomena of electrolysis need to be looked into very carefully before applying electrolytic methods to the determination of an atomic weight. The influence of the gases and vapours of the atmosphere has to be constantly kept in mind, as in the tendency to partial exchange of a halogen for oxygen when chlorides or bromides are heated in the air, the ready absorption of sulphuric acid, carbon dioxide, and ammonia from the atmosphere of a laboratory burning coal gas, &c.; in some cases the use of electric light and substitution of alcohol or well purified gasolene (free from the organic sulphur compounds of crude petroleum) for coal gas as fuel, may be advisable. The tendency of precipitated solids to carry down with them adherent soluble matter, and the slight solubility of many substances commonly counted as insoluble, must not be overlooked. The limits within which the best glass and porcelain of which laboratory vessels are made may be acted upon by water, acids and other agents demand attention; among recent investigations bearing upon this point may be mentioned those of Weber, Saur, Mylius and Foerster.§ In cases in which substances in the gaseous state are directly weighed, it may even be worth inquiring whether the weight can be sensibly affected by the presence of vapour of mercury from manometers, of heavy hydrocarbons from vaselene used to lubricate stopcocks, or of glycerol employed to prevent leakage at connections—McLeod‖ approximately determined the vapour of mercury in a flask of 1·9 litre containing air in contact with the metal at common temperature as ·09 to ·12 of a milligramme, this result being intermediate between the figures found by Hagen and Hertz; this on Lord Rayleigh's weighing of ·15358 grm. for about the same volume of hydrogen would be ·06 to ·08 per cent., or would change the resulting value for the density of oxygen from 15·884 to 15·894 or 15·897—in all probability the circumstances of contact with the mercury or other vaporisable material would make such a correction practically quite immaterial, and the suggestion may perhaps be looked upon as a merely speculative refinement, but the

* T. W. Richards—Proc. Amer. Acad. Arts and Sci., **26** (1891), 281—291.

† A. Leduc—*Comptes rendus*, **115** (1892), 42 and 43—*Bulletin de la Soc. Chim. de Paris*, 5 Mars, 1892, 144.

‡ G. Neumann and F. Streintz—*Bulletin de la Soc. Chim. de Paris*, 20 Août, 1892, 678.

§ *Berichte d. deutsch. chem. Gesellschaft*, **25** (1892), 70, 97 and 2494.

‖ Chem. News, **48**, 251.

chemist in pursuit of an atomic weight must take nothing for granted; he must be, like Pyrrho or one of his disciples, ἐφεκτικός τε καὶ ζητητικός.

4. *Choice as to the quantities of materials to be used.*—While this must depend in some degree upon the means of weighing at command, and upon the conditions of each reaction adopted, there are some decided advantages in working upon a scale a good deal larger than that common in everyday analytical processes; this was recognized and acted upon by Stas. An important point to be looked to is that there shall not be a very great difference between the weights of two substances to be determined when we wish to get the combining ratio between them; theoretically it would be best that the weights of the two should be approximately equal—it was this consideration that led the writer to adopt as one of the methods for determining the atomic weight of gold the ignition of trimethyl-ammonium aurichloride, since this salt contains about 50 per cent. of metallic gold. The plan of using large quantities of interacting substances, one of them in small excess, and after interaction determining the exact amount of that excess, is one of great value, and has already been referred to as first employed by Pelouze and adopted by Stas. By evaporation to a small bulk of a residual liquid containing the small excess of the substance to be finally determined, the delicacy of this method may be further increased. In some cases the nature of the process may be more favourable to the attainment of accurate results with large, in others with small quantities. Hence it is best to use *both* large and small quantities, calculating out the results separately, and noting any tendency to constant difference between them.

5. *Practical precautions as to accuracy in manipulation.*—The general nature of these precautions is of course quite the same as in ordinary chemical analyses, but they need to be carried out with a minuteness quite unusual. All mechanical operations should be made as simple as possible. Transfers of material from one vessel to another should be avoided whenever they can be dispensed with. Filtration is an undesirable process. Processes involving the escape of gas from a liquid should be carried out in closed vessels, or in vessels provided with suitable tubes and bulbs to catch any of the liquid carried off in the form of fine spray. Like precautions are necessary in the evaporation of a liquid, a process which can be carried on with very fair rapidity in a closed vessel, warmed from without, and through which a steady current of purified and dust-free air (or other suitable gas) is drawn without allowing it to bubble through the liquid. In the ignition of solids also, when volatile matter has to be driven off, special precautions are required to prevent mechanical loss of minute particles of the solid. Stas' arrangements

for observing the end of the precipitation of a haloid salt of silver furnish a good example of attention to optical details.

6. *Precautions in regard to weighings.*—As a matter of course, the balances used should be of the best construction, kept in thoroughly good order, and tested from time to time as to their fulfilment of the well known essential conditions. The weights should in all cases be personally checked by the chemist himself as to their agreement among themselves, and the real value of each piece determined in terms of some one of them. In cases requiring the use of so-called *absolute* weights a comparison with some well authenticated standard will be necessary; best in a public office of the first class, not trusting to the alleged standard of an instrument maker, and in such cases the exact chain of comparisons with the prototype standard of mass should be reported. Weighings should be made by the method of oscillations, and referred in all cases to a vacuum, either by actual weighing in empty space or by due correction for the volumes of displaced air in the condition existing at the time of the weighing. Nothing in connection with the use of the balance demands more scrupulous attention than the hygrometric condition of everything concerned. The use of an enclosing vessel, always the same, to contain both materials to be weighed and their immediate receptacles, such as crucibles, tubes, &c., counterpoised by another similar vessel, of exactly the same size and character of surface, is a practice having notable advantages.

7. *Measurement by volume of liquids or gases.*—The employment of vessels nicely adapted in size and form to the requirements of each special case, and calibrated, or having their calibration carefully checked, by the chemist himself, is highly important. The greatest difficulty encountered is that of accurately determining temperature. In the case of considerable volumes of gas this difficulty is very serious, and it requires but a little simple calculation to show how gravely an atomic weight, when based on results derived from gaseous measurement, may be vitiated by apparently small errors in the ascertainment of temperature.

8. *Calculation of results.*—It should be needless to say that the original facts of experiment are always to be reported in full detail, so that they may be afterwards used by anyone, in any form of calculation, and irrespective of any changes that may be made in other atomic weights. Two different methods of calculation have been chiefly used. In the one, the ratio between two substances combining or separating from each other is calculated independently for each single experiment made, and the method of least squares then applied to determine a mean value for the ratio, and the probable error of this mean. In the other, the results of all the individual

experiments are added together on each side, and the ratio deduced directly from the sums of the quantities of materials thus shown to have combined or separated. The latter method, adopted by Meyer and Seubert in their recalculation of the atomic weights of the elements, is probably to be preferred, not merely because it gives much less trouble, but because *constant* errors are nowadays so much more important than *casual* or *fortuitous* errors, that the method of least squares, which only properly applies to the latter, is out of place. As the absolute quantities of material used may in some cases tend to influence the results obtained, perhaps the best plan is to apply Meyer and Seubert's method separately to different *series* of experiments, namely to those involving large and to those involving small quantities of material—observing the degree of accordance of the results thus obtained. Of course the degree of concordance among individual results should always be exhibited. The most important question in connection with the calculation of results for any single atomic weight is that of the values to be assumed for the other atomic weights involved. It should always be stated what values for these *have* been assumed, but there remains the question how far the assumptions made are justified by all of our knowledge on the subject, and what influence these assumptions have upon the conclusion reached in the particular case in hand. Manifestly the list of elements should in principle be treated as a consistent whole, and from *all* the combining proportions among them which have been determined the most probable value for *all* the atomic weights should be calculated. The difficulty in the way of doing this, however, lies in the fact that our available *data* are all to some extent vitiated by errors, partly *constant*, partly *fortuitous* in character, and we are without means of separating the two classes—search for constant errors presupposes elimination of casual errors, and the attempt to properly distribute casual errors, and by the calculus of probabilities to ascertain the most probable value in each case, and its degree of probability, presupposes the elimination of constant errors. The principle in itself, however, is clearly correct of obtaining by the best means available as many independent ratios as possible for the combining quantities of as many elements as possible, and then discussing *together* the conclusions to be drawn from all of these as to the atomic weights of the elements in question. Professor F. W. Clarke, of Washington, D.C., undertook several years ago a general discussion on this principle of all existing *data* for atomic weights, but he has become convinced that there is too much uncertainty as to the relative confidence to be placed in the different *data* now available to admit of carrying out the undertaking in full. He says in a letter of recent date to the writer of this paper,—"At

present the *data* are not full enough or good enough for the general solution of the problem, which would involve dealing with normal equations containing at least 70 unknown quantities. It is, however, possible to apply the method to selected groups of ratios, such as Stas' ratios involving Ag, K, Na, Li, Cl, Br, I and S; and the result of the discussion ought to be the best result attainable. The method may also be used in the manner which I indicated yesterday, so as to furnish a criterion of accuracy in the case of a single element, such as P, Cr or Au." This important matter has been more fully noticed by Professor Clarke in a published paper "On the question of concordance in atomic weight determinations" in the American Chemical Journal, **13** (Jan., 1891), 34.* As the basis for a general revision of atomic weights we need a large accumulation of experimental *data*, all fairly comparable with each other on the ground of care and precision in their determination. This naturally leads to another suggestion, offered by the writer with diffidence, yet believed by him to be worthy of careful consideration.

9. *Advantage to be derived from the application of greater working force and ampler means than can be commanded by private individuals to the determination of atomic weights.*—The investigation of atomic weights requires special aptitude, and special training, on the part of the chemist, calls for special and often costly apparatus and material, is very toilsome, and very consumptive of time, and demands exemption from frequent interruption, and from surrounding conditions unfavourable to accuracy of work. There are but few individuals altogether favourably placed in these respects; they cannot singly accomplish a great deal, and, working apart, they waste much time and labour on preparations in duplicate for separate researches, which might quite well answer their purposes in common if they were associated in a single laboratory; results so obtained, moreover, are compared with difficulty as *data* for calculation, since the conditions of experiment, and the weight to be given to the results are almost always more or less different. May it not reasonably be asked whether a liberal portion of such funds for research as are administered by the Chemical and Royal Societies would not be well applied if devoted to the establishment of a laboratory, and

* The importance and the difficulty of obtaining concordant results for an atomic weight when combining ratios in various directions are employed has been fully recognized by Stas. In the early part of his first great paper he says,—"*J'ose affirmer, san crainte d'être démenti, que tout chimiste qui s'est livré à des recherches sur le poids des atomes,* S'IL A VARIÉ SES MÉTHODES, *s'il a cherché le poids de l'atome d'un corps en fonction du poids de l'atome de deux ou de trois corps différents, a rencontré les mêmes difficultés, les mêmes contradictions. Aussi ai-je éprouvé pendant longtemps bien de pénibles perplexités.*" *Bulletin de l'Académie Royale de Sciences de Belgique,* **10** (1860), 211 and 212.

the support for a few years of a small corps of competent chemists, for the sole purpose of thoroughly revising the whole list of atomic weights, with every precaution that could be devised to secure accuracy? If this were done, specially devised and constructed rooms might be made to afford conditions—particularly atmospheric conditions—far more favourable than can usually be found in a general laboratory. Expensive apparatus could be provided freely, in view of the economy due to repeated use in connection with different researches of such appliances as vacuum balances with electro-magnetic arrangements for shifting the weights, large vessels of platinum or gold, calibrated vessels of superior accuracy, glass apparatus constructed with carefully ground joints instead of india-rubber connections, &c. Rare and costly materials might be commanded to an extent beyond the means of most individuals. Analysts naturally fitted for such delicate work should be secured, for not to everyone is given the manipulative skill of a Berzelius or a Stas; constant practice in the same line of work would train their eyes and fingers to a degree rarely attained in connection with ordinary research; by exchange of parts in the same investigation their personal errors might be eliminated, or at any rate detected; and, having no other duties, their time would be used in the most advantageous way, while they would be free from interference by the work of others going on about them in objectionable form. From work carried on under such uniform and well determined conditions results would be secured comparable *inter se* on equal terms to an extent impossible for the results of individual and unconnected researches. As the natural or acquired gift of accurate manipulative skill is not always accompanied by equal scientific judgment, the devising of methods and general direction of the work would be better left in the hands of a committee of the most competent scientific chemists, who should also superintend, with needful clerical assistance, the calculation and publication of results. The actual results of experiment should of course be published in the most minute detail, and should from time to time be made the subject of general discussion before the Chemical Society, or some other public scientific body, so as to secure suggestions as to possible sources of error, and the means of detecting or removing them.

No utilitarian advantage could be expected from the adoption of such a plan; most of the atomic weights are already known with an approach to accuracy quite near enough for all ordinary industrial purposes, and even for most incidental uses in ordinary laboratory practice. But great advantage in a purely scientific point of view might be looked for from a really exact determination of *the one* set of purely chemical constants

10. *Final form of statement of results.*—It seems desirable, if general consent can be obtained for such a change of usage, that the term "atomic mass" be uniformly substituted for "atomic weight." This has been recently advocated by Prof. G. F. Barker* on the sound basis of the desirability that scientific terms common to physics and chemistry should have but one uniform meaning. The point is perhaps not a very important one for the chemist alone, since he rarely has occasion to use the word weight otherwise than as, in a slovenly way, synonymous with mass. But everyone admits that precision in language conduces to precision in thought, and, although the chemist may not very often come into contact with the distinction between mass and weight, it is well that he should recognise it. In one respect particularly is it advantageous that the proper term shall be used for a definite quantity of matter, namely for that quantity which constitutes the atom of a given chemical element. Instead of the ideas belonging to the time before Dalton, of purely relative amounts of indefinitely divisible matter, we have now clear conceptions of atoms, having constant mass for the same element, of determinable difference of mass in the case of different elements, the several masses and numbers of which regulate the composition of all known substances and the products resulting from interaction among them. The atomic theory has advanced far beyond the condition of a mere working hypothesis, on which chemists long stood with more or less uncertain feet; but, even if this were not so, considering it, to use a common metaphor, only as a scaffold, there is no good reason, so long as we stand on it and work from it, that we should be careless about tying our scaffold poles and nailing our planks.

Further, and lastly, it seems greatly to be desired that all atomic masses shall be expressed in terms of the mass of the hydrogen atom taken as unity. For a large part of the present century this has been the uniform practice amongst nearly all chemists, but within the last few years, since it has been generally admitted that the best experimental evidence we have is in favour of a figure for oxygen near to, but distinctly less than, 16, when hydrogen is taken as unity, several articles have appeared in the scientific journals urging that O = 16 be adopted as the basis, and hydrogen be represented by a fractional number a little greater than 1. Brauner, Ostwald, Dittmar, Noyes, F. P. Venable, and others have taken the ground in question; Meyer and Seubert have vigorously attacked it. This paper—already too long—would be still further unduly extended if a full discussion were attempted of all that has been said upon the subject. But the principal arguments that have been put forward in favour of adopting

* Presidential Address to the American Chemical Society, 1891.

as a basis (we cannot correctly call it a "unit," though that term has been applied to it) O = 16 may be summed up in a few words. It has been said that most of our values for the atomic masses of the elements are deduced from experimental *data* involving oxygen, but few directly involving hydrogen alone; hence such changes in the ratio of O : H as have been made of late years, and any further changes of this ratio in the future, must necessitate a re-calculation of all or nearly all the other numbers. But we may well hope to see the ratio of O : H fixed before long with the greatest attainable precision; much has lately been done in this direction by Cooke and Richards, Lord Rayleigh, Scott, Morley, Keiser, and others, though it is a pity that the methods used have not been more varied. And it is yet more to be hoped that other ratios to connect hydrogen with the rest of the elements by roads not leading through oxygen —such as Cl : H—Br : H—S : H—C : H—N : H—may before long be ascertained. Even if change in the value for oxygen *should* render necessary a re-calculation of the whole list, this is no result to be very greatly dreaded; all values dependent upon that of oxygen have simply to be increased or diminished by a definite small fraction; this will at any time be easily done, but for most of the purposes of the laboratory need not be done at all, since for everyday occasions approximate numbers are quite accurate enough. It has also been said that if we adopt the basis O = 16 many of the elements will be represented by integer numbers, or numbers very nearly approaching integers. This argument really cuts both ways, since the change in question will make some of the numbers approach more nearly to, but others depart more widely from integers. It carries with it, moreover, the suspicion of a lingering trust in Prout's hypothesis on the part of some who have proclaimed aloud their belief that this has been completely overthrown. As far as mere convenience in calculation is concerned, the "round numbers" can be perfectly well used for most common purposes without thus developing them by a formal change in the basis of the system. But the most objectionable argument put forth in favour of such change is that all these numbers are expressive of *ratios* only, that *any* figures are allowable which correctly express combining ratios, and that there are no reasons for using one set of figures rather than another save mere arithmetical convenience. This involves a grave error. In adopting as *unity* the mass of a single atom of any particular element, preferably that one of which the mass is the smallest,* we have reason to believe that we

* It has been said that,—"At present, the atomic masses of the elements given in our text-books are all relative, being expressed in terms of that of hydrogen, taken as unity. But it is evident that from these relative masses, the absolute atomic masses of all the elements can be obtained by simple multiplication so soon

express the mass of all the others in terms of this as a really existent, definite, and constant quantity of matter, so that in saying, the atomic mass of oxygen is 15·88, we distinctly state our belief that a single atom of oxygen consists of 15·88 times as much matter as a single atom of hydrogen, but if we say that the atomic mass of oxygen is 16, and an intelligent student asks us "16 what?" how are we to reply? O = 1, as Thomson made it, is intelligible; O = 10, as adopted by Wollaston, or O = 100, as adopted by Berzelius, is merely the same thing in another form; but O = 16 is without any ground of scientific reason. The suggestion that it be adopted is somewhat as if, a mètre having long been counted as about 40 inches long, and a mètre bar being a good deal in use for actual measurements, the true ratio between the mètre and the inch were ascertained, and it were then proposed to call the mètre a "quarantaine" and define the inch as 1·0151 fortieths of this. The analogy is not perfect, but illustrates not unfairly the confusion of thought in regard to units of measurements. In all really scientific use of the numbers representing the atomic masses of the elements, they should be referred to some one of them, preferably to that of hydrogen, as to a natural unit. The adoption of any other basis tends to confuse the consideration of any natural relations between these constants, as has been pointed out by Stas himself in reference to the hypothesis of Prout; numbers which on the basis of O = 16, come very near to integers, cease to do so when H is taken = 1, and O has assigned to it its true value as obtained by experiment.

In bringing this paper to an end, the writer wishes to express his thanks for aid in obtaining or verifying references, to his friends Prof. P. De Wilde, of the University of Brussels, Prof. F. W. Clarke, of the Chemical Department of the U. S. Geological Survey, Washington, Prof. Ira Remsen, of the Johns Hopkins University, Baltimore, and Prof. A. C. Hale, of Brooklyn, Secretary of the American Chemical Society, especially to Prof. De Wilde for valuable assistance in regard to the life and scientific work of Stas.

as we know the absolute mass of the hydrogen atom," with a calculation to show on certain assumptions, what fraction of a milligramme (itself but the millionth part of a kilogramme) represents the "absolute mass" of a hydrogen atom. All expressions of mass are relative, but, if we use the term "absolute mass," to which is it more properly applied, the mass of a hydrogen atom, fixed by nature, or that of a certain lump of iridio-platinum, set apart by human governmental decree, and stored in the *Bureau des archives* in Paris?

Bruxelles, le 18 février 1865.

Mon cher Collègue,

Je vous remercie de l'offre que vous
me faites de publier dans le Chemical
News les nouveaux mémoires sur les
poids atomiques que je viens de présenter
à l'Académie de Bruxelles. J'accepte
votre offre avec le plus grand plaisir.
Ces mémoires ne pourront être livrés
à l'impression que d'ici à trois mois
au plutôt; ils seront accompagnés de
figures qui demandent beaucoup de
temps pour être exécutées. A mesure
que les feuilles seront imprimées je
vous les expédierai.

Je ne sais si la forme que j'ai prise
pour la rédaction de ces nouveaux
travaux convient à une reproduction

dans votre journal. Vous jugerez vous
même s'il ne sera pas nécessaire de
faire des extraits ou des resumés plutôt
que de les reproduire textuellement.
Le travail que j'ai publié en 1862
n'était qu'un resumé. Les chimistes
qui ont eu l'occasion d'examiner avec
moyens de travailler et mes methodes
m'ont demandé d'exposer en detail
tout ce que j'ai fait en completé
dans ces cinq dernières années. Peut être
tout suffirait-il de reproduire l'intro-
duction que j'ai mise en tête des trois
mémoires. Dans cette introduction j'ai
exposé le but que j'ai poursuivi dans
les recherches et les resultats généraux
aux quels je suis arrivé
Dans le premier mémoire j'ai recherché
si les lois des proportions chimiques sont
des lois absolument exactes, ou simplement

des lois limites. Je suis arrivé, après de plus laborieux travaux que je crois aucun jamais été entrepris, à constater que ce sont des lois mathématiques comme depuis un demi siècle la chimie l'ont admis sans preuve. Je ne puis pas vous donner ici une idée de la méthode employée pour arriver à cette démonstration; vous comprenez qu'il reste que l'analyse et la synthèse qui nécessairement comportent une erreur sont impuissantes à donner la solution de ce problème. Je l'ai résolu par un principe nouveau, d'une grande simplicité, par constatation uniquement. Dans la recherche de la présence ou de l'absence de la matière, indépendamment du poids de celle-ci. Vous verrez plus tard combien les résultats ont été rigoureux.

Dans la deuxième mémoire j'ai recherché si le poids atomique de l'argent est réellement représenté par une constante lorsqu'on le réduit du bromure, du chlore et de l'iode.

j'ai exécuté dans cette intention des nouvelles
synthèses de l'iodure et du bromure d'argent
et des nouvelles analyses du bromate, du
chlorate et de l'iodate d'argent. A cette
occasion j'ai fait une revision des principes
sur lesquels les chimistes ont basé jusqu'ici
les synthèses et les analyses. Des nouvelles
méthodes donnent le moyen de mesurer
exactement l'erreur commise dans les
opérations.

Enfin dans le troisième mémoire j'ai
soumis à un contrôle nouveau mes travaux
sur l'azote, le chlore, le brome, le potassium,
le sodium, l'argent et j'y donne en outre
trente nouvelles recherches sur le tellure.
Ces nouvelles recherches confirment
absolument mes anciens travaux.
Vous verrez qu'après la publication de
ces mémoires il n'y aura peut-être un chimiste
qui ne basant sur l'expérience admettra
la loi de Prout.

J'accepte avec plaisir votre journal.

Recevez, mon cher Collègue, l'expression
de mes sentiments de haute estime et de dévouement

J. S. Stas

Monsieur,

Votre lettre du 7 de ce mois m'est parvenue hier seulement ainsi que votre mémoire sur le poids atomique de l'aluminium et le rapport de M. le Dr Kimball que vous m'avez fait l'honneur de m'adresser, et j'empresse de vous remercier. Puisque votre désir est que l'honneur de mettre à la poste à votre adresse leur soit à part de mon travail sur la détermination des rapports qui existent entre l'oxygène, les chlorures et les bromures alcalins, j'aurai plaisir, Monsieur, à accepter l'un de ces exemplaires comme un hommage d'admiration pour votre magnifique travail sur le poids atomique de l'aluminium et de vous bien faire parvenir l'autre exemplaire à M. le Dr Kimball, ainsi que la lettre jointe à la mienne.

Je connais depuis bientôt 8 années votre mémoire sur le poids atomique de l'aluminium et depuis plus de 30 années je savais que le poids atomique de ce métal déterminé par M. Dumas était faux, car un de mes premiers travaux a été l'analyse quantitative du chlorure d'aluminium que j'ai employé à plusieurs reprises pour mon Traité de Chimie

la présence des Chlorures de potassium
et de sodium en quantité très notable.
La doute pour moi n'était pas possible
sur la cause de l'erreur commise par
M. Dumas.

ayant attribué à une portion des expériences
faites par M. Dumas sur la densité
de l'oxygène par l'argent, j'ai fait sur
la demande exprès de tout nouveau
une série complète de toutes les
méthodes employées successivement
par moi pour une première détermination
pure et j'ai constaté l'exactitude
des indications données par moi au
sujet des caractères du métal pour
et j'ai constaté aussi que de l'argent
dans des circonstances données peut
retenir un grand nombre de fois son
volume d'oxygène, et circonstances
ne se présentent pas dans les conditions
dans lequel s'est trouvé l'argent
qui a servi à mes expériences, lesquelles
que quelle soit la quantité d'oxygène
occlus dans l'argent il suffit de le
fondre dans un courant d'hydrogène
pour les priver complètement.

Le long travail que j'ai exécuté
sur le sujet est terminé depuis
4 années; mais le temps et le mauvais
état de ma santé ne m'a pas

je désire publier en même temps,
à l'occasion d'une demande que m'a
faite en 1879 M. Lockyer, j'ai repris
mes recherches sur la perchlorisation. Dans le
but de m'assurer s'il est possible de la
procurer des chlorate et du perchlorate
de potassium sans exploser de la décomposer
par la chaleur en chlorure chlorhydrique
sans dégager en même temps un mélange
de chlore et de chlorure provenant
en même temps pour cette volatilisé
d'une toujours trace de résidu: silice,
alumine et silicate qui persistent à
la flamme le caractère sodique,
j'ai eu la chance de résoudre le problème
je suis parvenu à me procurer du
chlorate perchlorisé sans explosion de le
décomposer par la chaleur dans un
vase de platine, en chlorure chlorhydrique
sans mettre en même temps en liberté trace
de chlore. La chlorure qui se produit est
volatil sans résidu; le chlorate, le perchlorate
et le chlorure de potassium impur
mêlent à la flamme de l'hydrogène une pâle
coloration d'un bleu d'azur,
au lieu d'une coloration pourpre
comme on l'admet généralement. Mes
recherches sur la perchlorisation constituent
une petite partie d'un travail

général que j'ai entrepris pour soumettre
à l'expérience l'hypothèse de M. Leclerc
sur la possibilité de la fusion de l'hydrogène
que nous considérons comme simple,
nous avons obtenu des résultats qui tendent
à appuyer cette hypothèse, le titane,
le calcium, le strontium, le baryum,
le thallium, donnent, si on examine avec
attention, qu'on les place dans les
conditions convenables, on ne pourra pas
faire naître le spectre cannelé avec
les composés des métaux indiqués ci-
dessus, si ces composés ne renferment
pas du fluor ou de l'hydrogène
de plus que par l'action de la chaleur
ou de l'électricité, on peut compléter
les spectres, mais pour faire disparaître
des raies appartenant au fluorure
La destruction des métaux est donc
une illusion créée par l'imagination,
Dans les nouvelles que je continue
ici sur l'hydrogène, j'espère tous les produits
chimiques avec lesquels j'ai étudié
l'azote pour voir si on obtient
constamment le cannelé que je viens
de vous décrire, je vous tiendrai alors
pour vous des résultats imprévus.
Je suis très malade, le travail est
devenu une peine pour moi et depuis
j'ai 74 années! Je vous prie d'agréer
Mon cher ami, mes sentiments de haute

J. V. Mas

Hermann Kopp.

KOPP MEMORIAL LECTURE.*

(Delivered February 20, 1893.)

The Life Work of Hermann Kopp.

By T. E. Thorpe, D.Sc., F.R.S.

By the death of Hermann Kopp, a year ago to-day, the army of science lost one of its generals of division, and our own Society one of the oldest and most distinguished of the eminent company we are proud to call our Foreign Members. It is significant of Kopp's power and promise, and of the position that he so early won for himself in the commonwealth of science, that he should have been elected a Foreign Fellow of our Society so far back as 1849, when he was barely 32 years of age. With the exception of his illustrious colleague Bunsen, who is the *doyen* of the Forty, and whose jubilee as a Foreign Member we celebrated last year, and of the veteran Fresenius, who was elected in 1844, he was, at the time of his decease the Senior Member on the list.

As the end of the century draws near, one after another of the men who have made this century what it is are passing over to the majority. It was characteristic of Kopp, in whom humour and pathos were happily blended, that he should have taken leave of Hofmann, at what proved to be their last meeting, with the closing words of the song:—

> Der Herr im Himmel schenk ein gnädig End
> Uns letzen Zehn vom vierten Regiment.

It would seem as if, in the sunset of life, he had seen the shadow of a coming event. Both the friends have now submitted themselves to the strict arrest of the fell sergeant, and have gone

> to join
> The innumerable caravan which moves
> To that mysterious realm where each shall take
> His chamber in the silent halls of death.

The 19th century has witnessed an extraordinary expansion of that branch of science which it is the proper business and true function of this Society to foster. The history of learning can show no parallel to it. Contrast the condition of chemistry in the 18th century with its

* Chemical Society's Memorial Lectures, No. II.

position to-day. It is true there were giants in those days: Black, Scheele, Cavendish, Priestley, Lavoisier, are men never to be forgotten. But their merit rests not more on the number or magnitude of their discoveries than on the influence they exercised on an intellectual movement, which it is at once the privilege and the glory of this century to have furthered and accelerated. Indeed we venture to think that the dispassionate historian of this movement, who, with "the cold neutrality of an impartial judge," weighs and assesses the part which successive workers have had in its progress, will recognise in the giants of our own time—men whose names are familiar in our mouths as household words—the signs of a mental stature not only as great as, but possibly even greater than, that of the greatest of their predecessors.

The history of an epoch is the history of its leading men. They are the centrés and sources of intellectual energy. In them the ever-widening waves of mental progress have their origin, and it is under their vivifying influence that science and learning grow and spread.

Hence, therefore, we do well, from time to time, to gauge our gain in knowledge by contemplating the life work of the men who have influenced it, and who have stamped it with the marks of their power and individuality. It is this consideration that has induced your Council to see in the occasions which the stern act of death compels us to notice, opportunities, not only of recording our sense of reverence, esteem, and admiration for those who have so faithfully tended the lamp of learning, but also of tracing the immediate outcome of their labours, and of measuring its influence on contemporary science.

By the wish of your Council I appear this evening, on this, the first anniversary of the death of Kopp, to discharge what is to me a pious duty. Five-and-twenty years ago it was my good fortune as a student in Heidelberg to come into contact with Kopp, and to be influenced by his work and teaching.

To know Kopp was to love him, and to love him was, as Steele wrote of another, a liberal education. For to his friends he was ever ready to display the ample treasures of a mind rich not only in the lore of an ancient learning, but stored with the knowledge of a time of great achievement and of profound historical interest—the time which stretches from the closing years of Berzelius down to the final decade of the century; which covers the period of the grand movement which had its inception in the little laboratory on the banks of the Lahn, and which witnessed those memorable intellectual combats between the champions of opposing schools of chemical thought, the echoes of which are only faintly heard, if heard at all, by the student of to-day. Kopp's colloquial powers were admirable; like the Great

Lexicographer, he loved to fold his legs and have his talk out. His strong common sense; his vigorous, incisive thought; the range of his information of men and letters; his quick, retentive memory; his felicity of expression; his fund of anecdote; his ready wit and genial humour—all made him delightful to listen to. To watch the play of his features as he talked was in itself a recreation. Every line in the quaint impressive face was instinct with intelligence, the outward and visible sign of the active restless *geist* behind it. Not that there was any sense of unrest about the man. When I first knew him, a quarter of a century ago, he may be said to have passed the noontide of his intellectual career; he was living the quiet, contemplative, post-meridian life of a philosopher whose period of active service as a researcher was well nigh spent, happy in his surroundings and in his occupation; his social sympathies satisfied by his relations with colleagues like Bunsen, Kirchoff, Helmholtz, Renaud, Königsberger, and Zeller; and his mental activity finding scope for itself in his lectures, in the exercise of the various offices connected with the management of the University which he was called upon to fill, and in his literary labours. His life, like that of the greater number of men of science, had not been what the world calls eventful; the successive steps in his preferment as a teacher and the appearance of his books and memoirs were the main incidents which marked the even tenor of his way. Born October 30, 1817, at Hanau, he was early attracted towards the study of natural science. His father, Johann Heinrich Kopp, a distinguished physician, seems to have occasionally occupied himself with experimental chemistry, and Leonhard's *Taschenbuch* and Gehlen's *Journal* contain papers by him on mineral analysis, and on investigations relating to physiological chemical products. The younger Kopp received his school training at the gymnasium of his native town, where he acquired that knowledge of Latin and Greek, and that love for classical learning, which he turned to such signal account in the preparation of his great work on the History of Chemistry. When eighteen, he proceeded to Heidelberg, to the University which eventually claimed him as Professor, where he studied chemistry under Leopold Gmelin, and physics under Wilhelm Muncke. Gmelin, who became Ordinary Professor of Medicine and Chemistry in the University in the year in which Kopp was born, is mainly known by his *Handbuch der Chemie*, of which an English translation by the late Henry Watts, the first editor of our Journal, was published by the Cavendish Society. Muncke is chiefly remembered on account of his share in the production of Gehler's *Physikalisches Wörterbuch*, and by his work on the thermal expansion of liquids. Wöhler has told us something of the conditions under which practical chemistry was studied in Heidelberg during the first quarter

of the century, from which we may gather that Kopp could have had but few opportunities of gaining experience of manipulative work in the old cloisters which at that time did duty as the University laboratory. He left Heidelberg for Marburg, where he graduated in 1838, presenting to the Philosophical Faculty as his thesis an essay entitled, *De oxydorum densitatis calculo reperiendæ modo*, from which it is evident that he had already, whilst barely 21 years of age, been attracted by those problems which were to constitute the chief experimental labours of his life. From Marburg he passed to Giessen, drawn thither by the influence which has made the Giessen laboratory famous in the annals of chemistry. At Liebig's instigation, and under his direction, he studied the mode of decomposition of mercaptan by nitric acid. This, which was for the most part a repetition of the work of Löwig and Weidmann on ethylsulphonic acid and its salts, is, practically, the only investigation in pure chemistry that Kopp ever published. Work of this kind had evidently few attractions for him, and he quickly returned to those studies which, as his inaugural dissertation shows, he felt that he was most fitted to pursue.

In 1841 Kopp became a *privat-docent* in the Giessen University, lecturing alternately on theoretical chemistry, crystallography, meteorology, and physical geography. At about this time, that is, when 24 years of age, he began his *History of Chemistry*, and, as his material accumulated, he added this subject to the list of his lecture courses. In 1843 he became Extraordinary Professor, and on the removal of Liebig to Munich in 1852, he and Heinrich Will were together made Ordinary Professors, and were entrusted with the charge of the Giessen laboratory. But to a man like Kopp such a position was certain to prove uncongenial; he was not fitted, either by temperament or by training, to carry on the traditions of a place so indissolubly associated with the name and fame and field of work of another, and after a year he resigned the sole control to his friend and colleague. Kopp remained in Giessen nearly five-and-twenty years, and all his most important experimental work was done there. In 1863 he received a call from Heidelberg, which he accepted; here, as has been said, he remained until his death, occupying himself latterly with lectures on the history of chemistry and on chemical crystallography. He was repeatedly solicited to accept a position in some one of the larger universities, notably in Leipsic and in Berlin; but all attempts to draw him from his dear Ruperto-Carolina were unavailing. "Even Bunsen alone," he was wont to say, "keeps me fast in Heidelberg." And by no one is Kopp's departure more keenly felt than by Bunsen, his friend and colleague for more than a quarter of a century. The strollers on the Anlage still miss the

quaint figure on its way to the daily visit to the old veteran, who, rich in honour and in years, is now the last of that famous group which has made Heidelberg renowned as a centre of intellectual life and scientific activity.

Kopp is best known to the literary world by his *History of Chemistry*. The first volume of this work, a monument of learning and of patient labour, of constructive skill and sagacious criticism, appeared in 1843, and the fourth and final volume in 1847. His life-long friend Hofmann, who was with him at Giessen, has told us that, by the publication of this classical work, Kopp, then barely 30 years old, suddenly found himself famous :—"With one accord his contemporaries recognised that here was a production which, whether they regarded the thoroughness of research that it displayed, or the manner in which the material resulting from that research was sifted and arranged, was without a parallel in the literature of any other country. And even to-day, after the lapse of nearly half a century, there is no historical work on chemistry that can be even remotely compared with it. Numbers of books relating to the same subject, some of considerable merit, have since been published in Germany and France, but it is not difficult to perceive that they are all grounded on Kopp's great work." For upwards of 40 years Kopp had it in contemplation to bring out a new edition, and much of the later historical work he published, such as his *Beiträge zur Geschichte der Chemie*, which appeared between 1869 and 1875, and the *Entwicklung der Chemie in der neueren Zeit*, printed under the auspices of the Historical Commission of the Bavarian Academy in 1873, together with the two volumes on *Die Alchemie in älterer und neuerer Zeit*, grew out of the materials he had gathered together. "But," again to quote Hofmann, "the better is here the enemy of the good. Kopp postponed the 'vermehrte und verbesserte Auflage' year after year, in the hope of being able to make a fuller study of certain special periods. Whoever is familiar with the mass of profoundly interesting matter he had accumulated, or who has had the opportunity of seeing the bulky note-books in which it was stored, must deeply lament that the hand which could alone arrange these treasures is now stiffened in death."

On the death of Berzelius, in 1848, the leaders of the Giessen school determined to carry on the work which had mainly occupied the closing years of the illustrious Swedish chemist. Berzelius' *Year Book* had become a power in the chemical world, mainly on account of the authority wielded by the greatest chemical critic of his time. The *Jahresbericht* of Liebig and Kopp differed, however, fundamentally, both in plan and execution, from its Swedish prototype. It was to be a review of the year's progress, not only in

chemistry, but also in all those sciences which were associated with chemistry, or were, in any definite sense, ancillary to it; it was to be done impartially, and with no special reference to any set of dogmas or particular school of chemical thought. Practically the whole of the more active members of the scientific side of the Philosophical Faculty of the University were concerned in its production. To Kopp fell the greater share of the arrangement, and of the general editorial management; in addition, he undertook the summaries relating to Theoretical, Physical, and Inorganic Chemistry. To Buff and Zamminer were entrusted Pure Physics; to Heinrich Will, Organic Chemistry; to Knapp, Technical Chemistry; to Ettling, Mineralogy; and to Dieffenbach, Chemical Geology. The first volume appeared towards the close of 1849, and consisted of a review of the work of 1847 and 1848. Liebig continued to be associated with Kopp as editor for some years after his removal to Munich, but in 1857 his place was taken by Will, who acted as co-editor until 1862, when Kopp resigned his share in the responsible direction of the publication just prior to his removal to Heidelberg. No chemist active in the prosecution of research needs to be reminded of the value of the *Jahresbericht*. It has undoubtedly exercised a most beneficent influence on the development of chemical science in Germany, and it has been of the greatest service to those chemists in this country to whom German is not an unknown tongue. The attempt was made to introduce the *Jahresbericht* to English readers by means of a translation published under the direction of Hofmann and Warren De la Rue, but the good seed fell upon stony places, and after a year or two the enterprise was abandoned. Matters in 1849 were doubtless better with us than Liebig found them to be in 1837, when he told Berzelius that England was not the land of science, and that our chemists were ashamed to call themselves so because the apothecaries had appropriated the name.* Possibly the reason for the ill success of the venture is to be found in the fact that the Journals of this Society have, from the outset, taken note, in a more or less systematic way, of current chemical work in other countries. Be that as it may, there is practically no longer room for the German publication in this country;

* "Ich bin einige Monate in England gewesen, habe ungeheuer viel gesehen und wenig gelernt. England ist nicht das Land der Wissenschaft, es existirt dorten nur ein weitgetriebener Dilettantismus, die Chemiker schämen sich Chemiker zu heissen, weil die Apotheker, welche verachtet sind, diesen Namen an sich gezogen haben. Mit dem Volke war ich ausserordentlich zufrieden, Zuvorkommenheit, Gastfreiheit, kurz ich habe sonst an ihnen alle Tugenden gefunden. Graham macht auch in wissenschaftlicher Hinsicht die schätzbarste Ausnahme, es ist ein vortrefflicher Mensch, auch Gregory, der an seine Stelle in Glasgow gekommen ist."—Liebig to Berzelius, November 26, 1837.

since 1871 our Society has taken in hand an English *Jahresbericht*, and issues to its members monthly abstracts of all papers relating to, or bordering on, chemistry, in which, as regards fulness, comprehensiveness, and promptitude of publication, we have striven to emulate the example, and possibly even bettered the instruction, of our distinguished Foreign Member.

In 1851 Kopp joined Liebig and Wöhler in the production of the *Annalen der Chemie und Pharmacie*, and for many years he continued to take the responsible share in its management. His name as editor appears on the title-page of no fewer than 190 volumes of this famous periodical, which, under its present designation of *Justus Liebig's Annalen der Chemie*, constitutes an abiding monument to the influence and power of its great progenitor.

Kopp's services to the literature of our science were, however, by no means confined to its journalism. Engrossing and arduous as his duties as an editor must have been, he yet found time to write the admirable *Introduction to Crystallography*, and to prepare the section on "Theoretical Chemistry" in that well-known text-book, Graham-Otto's *Lehrbuch der Chemie*. These works enjoyed great popularity in Germany, and have exercised no inconsiderable influence on the education of the present generation of chemists in that country. The *Introduction to Crystallography* was indeed written specially for chemists with a view of interesting them in a study which is still too frequently neglected by them; and the "Theoretical Chemistry" proved of signal service in disseminating the doctrines which constituted the "new chemistry" of 30 years ago.

No record of Kopp's literary activity would be complete without a reference to his occasional writings, some of which are among the most typical and most characteristic of his productions; as, for example, his *Aus der Molecularwelt*, written for Bunsen's 70th birthday, and the *Aurea catena Homeri*, with which he greeted Wöhler when fourscore years of age In the *Molecularwelt*, Kopp's delicate fancy and quaint humour are seen at their best; the book attracted considerable attention even beyond chemical circles, and rapidly ran through a number of editions. His lecture *Sonst und Jetzt in der Chemie*, which appeared in 1867, may still be read with interest as an historical account of the changes which have conduced to the present development of chemical theory. His pen, indeed, in spite of frequent illness and waning strength, was busy to the last, and he closed a long half century of literary labour in preparing for Ostwald's "Chemical Classics," an annotated edition of Liebig and Wöhler's famous memoir on the radicle of benzoic acid—the memoir which, it will be remembered, Berzelius hailed as the dawn of a new day.

Kopp's scientific papers relating to his experimental and critical labours appeared mainly in *Poggendorff's Annalen* and in the *Annalen der Chemie und Pharmacie*. Two or three of his early communications were printed in the *Philosophical Magazine*, and his elaborate memoir on the specific heat of compound substances, in which he sought to develop Neumann's law, was published by the Royal Society. The following is a list of his papers :—

1. "Einfache Construction eines Differential-Barometers." *Pogg. Ann.*, **40**, 1837, 62—66.
2. "Ueber die Vorausbestimmung des specifischen Gewichts einiger Klassen chemischer Verbindungen." *Pogg. Ann.*, **47**, 1839, 133—152.
3. "Einiges über Löslichkeit." *Annalen*, **34**, 1840, 260—271.
4. "Ueber das Volumenometer, ein Instrument zur Bestimmung des Volums fester oder flüssiger Körper." *Annalen*, **35**, 1840, 17—43.
5. "Ueber die Cohäsion einiger Flüssigkeiten." *Annalen*, **35**, 1840, 230—234.
6. "Ueber die Zersetzung des Mercaptans mit Saltpetersäure." *Annalen*, **35**, 1840, 343—350.
7. "Ueber Atomvolum, Isomorphismus und specifisches Gewicht." *Annalen*, **36**, 1840, 1—32.
8. "Ueber die Verhältnisse zwischen Atomgewicht und specifischen Gewicht bei festen und flüssigen Körpern." *Annalen*, **40**, 1841, 173—182.
9. "Ungleiche Mischung von Metall-Legirungen in geschmolzenem Zustande." *Annalen*, **40**, 1841, 184—186.
10. "Dichtigkeit des Cadmiumamalgams." *Annalen*, **40**, 1841, 186.
11. "Ueber die Löslichkeit des Kochsalzes in wässrigem Weingeist." *Annalen*, **40**, 1841, 206.
12. "On the Atomic Volume and Crystalline Condition of Bodies." *Phil. Mag.*, **18**, 1841, 255—264.
13. "Ueber die Volumtheorie." *Pogg. Ann.*, **52**, 1841, 243—261.
14. "Ueber die Abhängigkeit der Krystallform von Atomvolum und über die Aenderung derselben durch Erwarmung." *Pogg. Ann.*, **52**, 1841, 262—267.
15. "Ueber das verschiedene Verhalten der verschiedenen Mischungen aus Alkohol und Wasser in Bezug auf Dichtigkeit." *Pogg. Ann.*, **53**, 1841, 356—362.
16. "Ueber Isomorphismus analoger Verbindungen ohne Isomorphismus der entsprechenden Bestandtheile." *Pogg. Ann.*, **53**, 1841, 446—458.

17. "Bemerkungen über die Volumtheorie und L. Gmelin's Atomzahlentheorie." *Pogg. Ann.*, **54**, 1841, 202—207.
18. "Recherches sur le volume spécifique." *Annales de Chimie*, **4**, 1842, 462—508.
19. "Sur un volumenomètre." *Annales de Chimie*, **6**, 1842, 380—382.
20. "Sur un nouveau baromètre raccourci portatif." *Annales de Chimie*, **6**, 1842, 383.
21. "Ueber die Vorausbestimmung einiger physikalischen Eigenschaften bei mehreren Reihen organischer Verbindungen." *Annalen*, **41**, 1842, 79—89, 169—189.
22. "Notiz über einige chromsaure Salze." *Annalen*, **42**, 1842, 96—103.
23. "On a great Regularity in the Physical Properties of Analogous Organic Compounds." *Phil. Mag.*, **20**, 1842, 187—197.
24. "Ueber die Berücksichtigung der Temperatur bei vergleichung der specifischen Volume." *Pogg. Ann.*, **56**, 1842, 371—392.
25. "Ueber das abgekürtze Barometer." *Pogg. Ann.*, **56**, 1842, 513—541.
26. "Recherches sur les températures où les volumes spécifiques des différentes substances sont comparables." *Annales de Chimie*, **7**, 1843, 389—401.
27. "Ueber den Verbindung nach Volumen von Aether mit Wasser zu Alkohol." *Annalen*, **46**, 1843, 215—221.
28. "Ueber den Zusammenhang zwischen der chemischen Constitution und einigen physikalischen Ergenschaften bei flüssigen Verbindungen." *Annalen*, **50**, 1844, 17—144.
29. "Ueber Siedepuncts-Regelmassigkeiten und daraus abgeleitete Folgerungen, so wie über Theorie der specifischen Volume der Flüssigkeiten." *Pogg. Ann.*, **52**, 1844, 283—316.
30. "Uebersicht der Resultate einiger Arbeiten, welche Regelmässigkeiten in den specifische Gewichten und den Siedepuncten chemischer Verbindungen behandeln." *J. pr. Chem.*, **34**, 1845, 1—36.
31. "Ueber die Siedepuncte einiger isomerer Verbindungen, und über Siedepuncts-Regelmässigkeiten überhaupt" *Annalen*, **55**, 1845, 166—200.
32. "Point d'ébullition des combinaisons organiques." *J. Pharm.*, **9**, 1846, 222—224.
33. "Berichtigung einer Angabe über chromsaures Zinkoxyd und Kupferoxyd." *Annalen*, **57**, 1846, 386—388.
34. "Bemerkungen zu Löwig's Volum-theorie." *Pogg Ann.*, **59**, 1846, 506—525.

35. "Untersuchungen über das specifische Gewicht, die Ausdehnung durch die Wärme und den Siedepunct einger Flüssigkeiten." *Pogg. Ann.*, **72**, 1847, 1—62, 176, 223—293.

36. "Ueber das Atomgewicht des Siliciums und die atomistische Zusammensetzung der Kieselerde." *Annalen*, **67**, 1848, 356—359.

37. "Ueber die specifische Wärme einiger Flüssigkeiten." *Pogg. Ann.*, **75**, 1848, 98—108.

38. "Ueber Siedepuncts-Regelmässigkeiten und H. Schröder's neueste Siedepuncts-Theorie." *Pogg. Ann.*, **81**, 1850, 374—402.

39. "On the Relations between the Chemical Composition and the Boiling Points and Specific Volumes." *J. Chem. Soc.*, **3**, 1851, 104—105.

40. "Ueber die Ausdehnung einiger fester Körper durch die Wärme." *Annalen*, **81**, 1852, 338—340.

41. "Ueber die specifischen Volume flüssiger Verbindungen." *Annalen*, **92**, 1854, 1—32.

42. "Ueber die Volumänderung einiger Substanzen beim Erwärmen und Schmelzen." *Annalen*, **93**, 1855, 129—232.

43. "Ueber die Bildung von Krystallen mit Kernen." *Annalen*, **94**, 1855, 118—125.

44. "Ueber die Abhängigkeit des Siedepuncts und des specifischen Volums flüssiger Verbindungen von der chemischen Zusammensetzung." *Annalen*, **95**, 1855, 121—126.

45. "Beiträge zur Stochiometrie der physikalischen Eigenschaften chemischer Verbindungen." *Annalen*, **96**, 1855, 1—36, 153—185, 303—335; **100**, 1856, 19—38.

46. "Untersuchungen über das specifische Gewicht, die Ausdehnung durch die Wärme und den Siedepunct einiger Flüssigkeiten."

47. "Relations entre la composition chimique et le point d'ébullition et la densité des combinaisons fluides." *Compt. rend.*, **41**, 1855, 186—190.

48. "Mémoire sur les changements de volume qui accompagnent l'élévation de température et la fusion." *Annales de Chimie*, **47**, 1856, 291—296.

49. "Ueber die specifischen Volume stickstoffhaltiger Verbindungen." *Annalen*, **97**, 1856, 374—376.

50. "Ueber die Siedepuncte entsprechender Brom- und Chlorverbindungen und die Formeln der Silicium- und Titanverbindungen." *Annalen*, **98**, 1856, 265—272.

51. "Sur quelques régularités dans les points d'ébullition des combinaisons organiques." *Annales de Chimie*, **49**, 1857, 338—364.

52. "Recherches sur les volumes spécifiques des combinaisons liquides." *Annales de Chimie*, **15**, 1857, 458—486.
53. "Sur le calcul des densités de vapeur." *Compt. rend.*, **44**, 1857, 1347—1348.
54. "Zur Erklärung ungewöhnlicher Condensationen von Dämpfen." *Annalen*, **105**, 1858, 390—394.
55. "On the Relation between Boiling Point and Composition in Organic Compounds." *Roy. Soc. Proc.*, **10**, 1859–60, 463—467.
56. "Krystallochemische Notizen." *Annalen*, **125**, 1863, 369—374.
57. Ueber die specifische Wärme starrer Körper, und Folgerungen bezüglich der Zusammengesetztheit s.g. chemischer Elemente." *Annalen*, **126**, 1863, 362—373.
58. "Zur Lehre von den specifischen Volumen flüssiger Verbindungen." *Annalen*, **128**, 1863, 193—200.
59. "Sur la chaleur spécifique des corps solides; déductions relatives à la nature composée des corps considérés comme éléments." *Compt. rend.*, **56**, 1863, 1251—1255.
60. "Considerazioni sulla differenza esistente fra la forza elastica del vapor acqueo e la forza elettromagnetica nella loro applicazione come motori Majocchi." *Ann. Fis. Chim.*, **20**, 1845, 201—207; *Il Cimento*, **3**, 1845, 225—234.
61. "Investigations on the Specific Heat of Solid and Liquid Bodies." *Roy. Soc. Proc.*, **13**, 1864, 229—239.
62. "Bemerkungen zur specifisches Gewicht des Benzols." *Ann. Chem. Pharm.*, **5** (Suppl. Bd.), 1867, 303—315.
63. "Ueber die Siedepuncte der Kohlenwasserstoffe C_nH_{2n-6}." *Ann. Chem. Pharm.*, **5** (Suppl. Bd.), 1867, 315—328.
64. "Mémoire sur les volumes moléculaires des liquides." Heidelberg, 1886.
65. "Ueber die Molecularvolume von Flüssigkeiten." *Annalen*, **250**, 1889, 1.

Compared with those of his great contemporaries Liebig and Wöhler, the number of his scientific papers may seem small. But, in estimating Kopp's industry and power of work as an investigator, the character of his experimental researches must be considered. The nature of the relations which he strove to elucidate often necessitated the determination of the physical constants of some scores of substances, many of which could only be prepared in a state of sufficient purity by lengthy operations. Moreover, these innumerable measurements were not only troublesome and tedious in themselves, but they were followed, very frequently, by long and

wearisome calculations. The rich field of chemical physics will indeed only yield its fruit by patient and incessant tillage.

Kopp occupies an almost unique position as an investigator. The one consistent purpose of his work was to establish a connection between the physical and chemical nature of substances; to prove, in fact, that all physical constants are to be regarded as functions of the chemical nature of molecules. It is not implied, of course, that the conception of such an intradependence originated with him. As a matter of fact, almost immediately after the publication of Dalton's *New System of Chemical Philosophy*, in which the doctrine of atoms was revived to account for the fundamental facts of chemical union, the endeavour was made to connect the chemical attributes of a substance with one of its best defined physical constants, viz., its atomic mass. Prout's hypothesis is, in reality, the generalised expression of such an attempt; it is an adumbration of Mendeléeff's great discovery of the Law of Periodicity. But it may be justly claimed for Kopp that no one before him made any systematic effort to connect such of the physical qualities of substances as admit of quantitative statement with the stochiometrical values of such bodies. The sporadic attempts made prior to 1840 were practically fruitless on account of the imperfect nature of the physical data up to to that time extant.

When Kopp began his inquiries, very few boiling points were known, even approximately; and he had, as a preliminary step, to ascertain the conditions under which such observations must be made in order that accurate and comparable results could be obtained. The thermal expansions of barely half a dozen liquids had been measured, and the very methods of making such measurements with precision had to be worked out.

At the outset of his investigations, Kopp found the physical constants with which he was more immediately concerned very much as Berzelius found Dalton's values of the relative weights of the atoms; at the close of his work, they were hardly less accurately known than were those stochiometric numbers to the ascertainment of which the great Swedish chemist had dedicated his life.

It would be quite impossible within the limits of such an address as this to attempt to give an analysis of each of Kopp's memoirs. I must, therefore, content myself with essaying to lay before you a generalised statement of the main outcome of his work, and of the development which it has received at the hands of his successors. Fortunately for the purpose of such a summary, Kopp's more important memoirs readily and naturally fall into comparatively few groups:—viz., (1) those concerning the relations between the specific gravities of substances and their molecular weights; (2) those treat-

ing of the relations between boiling point and chemical composition; and (3) the papers relating to the specific heats of solids and liquids. As regards the other papers, only the briefest notice is here possible.

In the paper on Solubility (*Annalen*, **34**, 260 (1840)), Kopp seeks to determine the behaviour of a solvent towards a mixture, in excess, of two soluble salts, or, in other words, to ascertain how far the solubility of one substance is affected by the presence of another when the conditions are such that chemical change is *a priori* impossible. Are the salts, he asks, dissolved in the ratios of their specific solubilities; or is the solubility of the one salt unaffected by the presence of the other; or can the aggregate amount of the dissolved saline matter be deduced from the specific solubilities of the constituents? He finds, as regards the solubility of two salts possessing a common basic radicle, that they are never present in the saturated solution in the exact amount required by their specific solubilities. In the case of two salts containing an acid radicle in common, it was observed that the salt having the "stronger" base preserved its specific solubility, and that the other salt dissolved in the solution to an extent depending on its particular character, the quantity being sometimes greater and sometimes less than the calculated amount He also shows how such determinations afford a method of recognising the existence of double salts in solution, but which, as in the well known case of carnallite, are more or less decomposed on crystallisation. Lastly, he points out how the temperature corresponding to the change of hydration, or some other condition, in a salt, either in the dissolved or undissolved portion, as, for example, in the case of sodium sulphate, may be deduced from the formulæ expressing the relation of solubility to temperature, where, as in that salt, we have to do with two solubility curves.

This investigation is noteworthy as being the precursor of the extensive inquiries which we owe to Karsten, Hauer, Rüdorff, and Engel. In the note on the Solubility of Common Salt in aqueous Alcohol of different strengths (*Annalen*, **40**, 266), Kopp opens up a field of labour which, 20 years later, taxed the energies of Schiff and Gerardin. No general law as to the partition of a soluble substance between two solvents, or as to the action of a mixture of two mutually miscible liquids in one of which the substance is insoluble, has hitherto been traced.

In the short paper on the Cohesion of Liquids (*Annalen*, **35**, 230), he describes a simple method for the quantitative estimation of the resistance which liquids offer to rupture. The power which a liquid possesses of resisting any tendency to internal separation of its parts has hitherto received but scant attention from physicists, presumably on account of the experimental difficulty of the problem. It is,

as shown by Donny, Osborne Reynolds, and Worthington, more considerable than we are apt to imagine, and is indeed comparable with that of solids. It would be interesting to submit Kopp's method to a careful experimental criticism, for it is so easy of execution that, if found accurate, valuable data could rapidly be accumulated by its aid.

In the paper "Ueber die Bildung von Krystallen mit Kernen" (*Annalen*, **94**, 118 (1855)), Kopp describes a characteristically ingenious method of throwing light upon the mode in which natural crystals are made to enclose foreign substances, as in the case of fluorspar, which frequently surrounds cubes of iron pyrites, and where, too, as is obvious from the nature of the cleavage, no very firm adhesion exists between the substances. The plan consisted in coating the crystal to be enclosed with a thin film of coloured collodion and then placing it in a solution of the salt which was to surround it. In spite of Kopp's interest in chemical crystallography, which under his direction became a most fascinating study, he only published a couple of notes on the subject; in the first he treats of the pleomorphism of magnesium sulphate, and in the second he discusses the bearing of analogous atomic composition on crystalline form (*Annalen*, **125**, 369 (1863)).

In nothing was Kopp's originality or ingenuity more strikingly manifested than in the construction of his apparatus. To a great extent he was his own instrument maker, and his materials were, for the most part, glass and cork. But no Japanese worker, with his few and primitive tools, ever produced results which, in point of delicacy, finish and accuracy, surpassed those which Kopp obtained by means of simple contrivances. It is told of Wollaston that when a distinguished foreigner called to see his laboratory, he had his chemical utensils brought in on a tray. "This," said he, "is all the laboratory I possess." I will venture to say that the whole of the apparatus which Kopp employed in the course of his researches on physical chemistry could be put on a very much smaller tray than must have been needed to hold the furniture of Wollaston's laboratory.

Kopp's first contribution to the literature of science consisted of an account in *Poggendorff's Annalen*, done when he was a student at Marburg, of a differential barometer which he had constructed (*Pogg. Ann.*, **40**, 62 (1837)). His volumenometer (*Annalen*, **35**, 17 (1840)) is an improvement on the stereometers of Say, Leslie, and W. H. Miller, not so much in simplicity of construction or of use, as in the greater convenience of its form, and in the more accurate results it is capable of affording. It may be readily made with materials ordinarily found in laboratories, and is especially useful for the

determination of the specific gravities of such substances as sugar, starch, silk, cotton, wool, flax, &c.

His ingenuity is further seen in his method (*Annalen*, **81**, 1 (1852)) of determining the thermal expansion of substances which, like sulphur, galena, zinc blende, fluorspar, &c., can only be obtained in irregular fragments and frequently of no great size. Much of our knowledge respecting the thermal expansion of minerals is in fact based on Kopp's work.

Closely related to this memoir is that on the change of volume which substances experience in passing from the solid to the liquid state (*Annalen*, **94**, 129 (1855)). With the exception of the work of Réaumur, in 1726, which was only qualitative in character, practically nothing was known on this subject prior to Kopp's investigation. By means of an apparatus which is simplicity itself and which could be put together in a few moments, Kopp determined the relation of the volume, when solid to that when liquid, of a large number of substances, such as ice, phosphorus, sulphur, stearic acid, calcium chloride, sodium thiosulphate, &c. The value of the apparatus lay, however, not so much in its simplicity as in the skilful work put into it, and in the exactitude of the results which came out of it. Although subsequent workers have had occasion to repeat Kopp's observations by other and far more elaborate apparatus, as, for example, that of Pettersson, the substantial accuracy of his observations has not been challenged. The main conclusions which may be drawn from his work are now the common property of the text-books. As a rule, the expansion coefficient of a solid substance increases very rapidly in the neighbourhood of the melting point, the most striking exceptions being phosphorus and ice. The increase in volume which a substance experiences in passing from the solid to the liquid condition depends, for the most part, on this rapid increase in the expansion coefficient and on the sudden expansion at the moment of melting. In some substances, like phosphorus, the change in the expansion coefficient is small, but the increase due to liquefaction is comparatively great; in wax, on the other hand, the increase in volume is mainly due to the change in the coefficient of expansion. Kopp was particularly attracted by the extraordinary behaviour of Rose's fusible metal, which had already been the subject of a careful examination by Erman in 1827. This alloy —a mixture of 2 parts of bismuth, 1 part of lead, and 1 part of tin— expands on warming from 0° to 59° in the ratio of 1 to 1·0027, but on further heating contracts, until at 82° it occupies the same volume as at 0°; it continues to contract until 95°, when its relative volume is 0·9947; it melts between 95° and 98°, when its volume suddenly becomes 1·0101. The nature of alloys had always a special interest

for Kopp, and two of his shorter papers ("Ungleiche Mischung von Metall-Legirungen, &c., *Annalen*, **40**, 184 (1841), and "Dichtigkeit des Cadmium-Amalgams," *Annalen*, **40**, 186 (1841) had reference to this subject.

Kopp, as an investigator, will be mainly known hereafter by his attempts to connect the physical constants of substances with their molecular weights and chemical composition. The greater number of his memoirs indeed are concerned with these relations. As already stated, his earliest paper on the subject was the dissertation he presented for his doctorate to the Philosophical Faculty of the University of Marburg.

I shall first treat of his work on the specific heats of bodies; then of his attempts to connect the boiling points of liquids with their chemical nature; and, lastly, with his long-continued efforts to trace the relations between the volumes and molecular weights of substances.

In 1818 Dulong and Petit found that when the atomic weights of the elements are multiplied by their respective specific heats approximately the same number is obtained. This fact was subsequently embodied by them in the statement that: "The atoms of all simple bodies have exactly the same capacity for heat." In 1831 this generalisation was extended by Neumann (*Pogg. Ann.*, **23**, 1) so as to include compounds, and what is now known as Neumann's law was thus expressed by its discoverer: "In bodies of analogous chemical composition the specific heats are inversely as the stochiometrical quantities, or, what is the same, stochiometrical quantities of bodies of analogous chemical composition have the same capacity for heat."

Subsequent observers, among whom may be named Avogadro, Hermann, and especially Regnault, Person, and Pape, added greatly to the experimental material on which the validity of Neumann's law is founded. The whole question was, however, reopened by Kopp in 1864. By means of a simple modification of the method of mixtures, Kopp determined the specific heats of a large number of substances, for the most part compound in their nature. He concluded that each solid substance, at a sufficient distance from its melting point, has a specific heat which may vary somewhat with physical conditions (temperature, greater or less density, amorphous or crystalline nature, &c.); but the variations are never so great as must be the case if a variation in the specific heat of a substance is to be held as a reason for explaining why the determinations of the specific heats of solid elements do not even approximately obey Dulong and Petit's law, nor those of solid compounds of analogous chemical constitution Neumann's law. Neither law is universally

valid, although Kopp found that Neumann's law applies in the case of many compounds of analogous composition to which, on account of their totally different chemical deportment, different formulæ are assigned; and even in cases in which these laws have hitherto been considered as essentially true the divergences from them are material. Each element has the same specific heat in its solid free state as in its solid compounds. From the specific heats to be assigned to the elements, either directly from experimental determination, or indirectly by calculation on the basis of the law just stated, the specific heats of their compounds may be calculated.

Kopp concludes his memoir with certain suggestive considerations as to the nature of the chemical elements. What substances, he asks, are to be regarded as chemical elements? Does the mere fact that they are non-decomposable determine this? Or may a body be non-decomposable in point of fact, and yet from reasons of analogy be regarded not as an element but as a compound? He reminds us that the history of chemistry furnishes numerous examples of cases in which sometimes one and sometimes another mode of view led to results which at present are regarded as accurate. The earths were non-decomposable in point of fact in 1789, when Lavoisier expressed the opinion that they were compounds, oxides of unknown metals. Lavoisier's argument was based on the fact that the earths enter as bases into salts, and that it was to be assumed in regard to all salts, that they contained an oxygen acid and an oxygen base. But the view, founded on the same basis, that common salt contains oxygen, and the subsequent view that what is now called chlorine contained a further quantity of oxygen besides the elements of an oxygen acid, did not find an equally permanent recognition. On the basis of the actual non-decomposability of chlorine, Davy, about 1810, maintained its elementary character; and this view became general when Berzelius adopted it, more, Kopp thinks, because he was outvoted than because he was convinced.

It cannot be maintained that the bodies which chemists regard as elements are absolutely simple substances. How far a body is to be regarded as an element is so far relative that it depends on the development of the means of decomposition which practical chemistry has at its disposal, and on the trustworthiness of the conclusions which theoretical chemistry can deduce. A discussion as to whether chlorine or iodine is an elementary substance can be taken only in the sense whether chlorine is as simple a body as oxygen or manganese, or nitrogen; or whether it is a compound body, as peroxide of manganese or peroxide of hydrogen, for example.

If Dulong and Petit's law were universally valid, it could be used as a test for the elementary nature of a substance whose atomic

weight was known. That iodine, from a direct determination, and chlorine, by an indirect determination of specific heat, had atomic heats agreeing with Dulong and Petit's law would be a proof that iodine and chlorine, if compounds at all, are not more so than other so-called elements for which this law is regarded as valid.

According to Neumann's law, compounds of analogous molecular composition have approximately equal molecular heats. In general, compounds whose molecule consists of a large number of undecomposable atoms, or is of more complex constitution, have greater molecular heats; especially in those compounds all of whose elements follow Dulong and Petit's law, is the magnitude of the molecular heat a measure of the complexity. If Dulong and Petit's law were universally valid, it might be concluded with great certainty that the so-called elements, if they are really compounds of unknown simple substances, are compounds of the same order. If we start from the elements at present assumed in chemistry, we must rather admit that the magnitude of the molecular heat of a body depends not only on the number of elementary atoms contained in one molecule of it, or on the complexity of its composition, but also on the atomic heat of the elementary atoms entering into its composition. It is possible that a decomposable body may have the same atomic heat as a non-decomposable one.

In a very great number of compounds the molecular heat gives more or less accurately a measure of the complexity of their composition, and this is also the case with those compounds which, from their chemical deportment, are comparable with the undecomposed bodies.

If ammonium or cyanogen had not been decomposed, or could not be so by the chemical means at present available, the greater molecular heats of their compounds, compared with those of analogous chlorine or potassium compounds, and the greater molecular heats of ammonium and cyanogen obtained by indirect determination, as compared with those of potassium and chlorine, would indicate the compound nature of these so-called compound radicles. The conclusion appears legitimate that, for the so-called elements, the directly or indirectly determined atomic heats are a measure of the complexity of their composition (*Phil. Trans.*, 1865, 155).

These conclusions are, it should be stated, largely based upon the fact of the abnormally low atomic heats of bodies of low atomic weight, such as carbon, silicon, boron, glucinum, &c., when taken at comparatively low temperatures. Kopp would regard bodies of low atomic weight as of a low order of complexity. But since it has been recognised that the specific heat of such bodies is very largely affected by temperature, and in such manner that their atomic heats

at high temperatures more and more closely approximate to the value required by Dulong and Petit's law, the force of Kopp's argument is materially weakened.

In 1841, Kopp, from observations on methyl and ethyl derivatives, drew attention to the fact that in many analogous chemical compounds the same difference in composition frequently occasions the same difference in boiling point (*Annalen*, **41**, 87, *et seq.*). He also pointed out that in many other similar compounds, mostly alcohols, acids, and esters of the fatty series, a difference of $x CH_2$ apparently corresponds to a difference of about $x19°$ in the boiling point; that an acid boils 40° higher than the corresponding alcohol; and that an ester boils 82° lower than the isomeric acid. On comparing analogous compounds differing only in the number of C atoms, he further concluded that the boiling point of the compound having xC atoms more than the other was $x \times 29°$ higher, and that a compound having xH atoms more than the other boiled $x \times 5°$ lower. He subsequently found that this difference of 19°, corresponding to an increment of CH_2, is not observed in all homologous series. Thus, in the benzene hydrocarbons $xCH_2 = x24°$; in the fatty ketones and aldehydes it is 22°; in the alkyl chlorides it is 31°; and in the fatty anhydrides it is 12·5°. Isomeric compounds of the same type and of the same chemical character have the same boiling point; if of the same type but of different character, or if of different type, their boiling points are different. Hence Kopp concluded that the boiling point of a liquid was a function partly of molecular weight and partly of chemical constitution. The influence of molecular weight, alone, may be studied by comparing bodies of strictly analogous constitution, *e.g.*, the normal fatty acids. If Kopp's main contention is valid, the relations should hold good at other temperatures than that of the boiling point under atmospheric pressure, and by observations on the vapour pressures of the normal fatty acids, Landolt concluded that such was the case.

Further and more accurate observations showed, however, that Kopp's original propositions must be materially modified. Wanklyn found that the increment for CH_2 in an homologous series became less and less as the series was ascended. Schorlemmer (*Phil. Trans.*, **172**, 123 (1872)) observed that in the homologues of marsh gas, the difference corresponding to CH_2 appears to become steadily less by 4° until it reaches the value 19°. Linnemann (*Annalen*, **162**, 39), by means of his well-known fractionating apparatus, determined with great accuracy a number of boiling points of members of correlated groups of fatty compounds, from which he concluded that equal differences in chemical composition do not give rise to equal differences in boiling point, but that the differences diminish, at least in

the lower members of the greater number of the series, as the series is ascended. Series, however, are known, as for example the alcohols, in which the differences for CH_2 are approximately constant; in some too, the differences increase as the series is ascended. Schumann, in 1881, studied the vapour pressures of esters of the fatty acids, from which he deduced conclusions in harmony with those of Landolt on the fatty acids in so far as they showed that the relations obtained were independent within certain limits of the magnitude of the pressure. At the same time, the relations themselves lent no support to Kopp's general conclusions.

The observations on boiling points which have accumulated since the time of Linnemann have confirmed the conclusions put forward by him. In homologous series the boiling point differences may either increase or decrease, or may vary irregularly as the series is ascended. Although in all cases it is not yet possible to assign causes for the apparent irregularities, these may to some extent be explained by considerations recently advanced by Dobriner and extended by Lossen.

It is possible to regard any three consecutive homologues containing carbon, hydrogen, and oxygen as methyl, ethyl, and propyl compounds. For example, the first three members of the series of normal fatty alcohols may be written:

MeOH,
EtOH,
PrOH.

Formulating the compounds in this way, Dobriner would term them a triad of oxygen compounds of the alkyls, for in each case the alkyl group is linked to oxygen. If, however, ethyl alcohol be taken as the initial member of the triad, the formulæ of ethyl, propyl, and butyl alcohols would be

$MeCH_2OH$,
$EtCH_2OH$,
$PrCH_2OH$,

and as here the methyl, ethyl, and propyl groups are linked to carbon, the triad would be spoken of as one of "carbon compounds" of the alkyls. Calling the difference between the boiling points of the methyl and ethyl compounds of any triad the "first boiling point difference," and that between the boiling points of the ethyl and propyl compounds the "second boiling point" difference, Dobriner deduced the following two rules:—In any triad of oxygen compounds the first difference is less than the second. In any triad of carbon compounds the first difference is greater than the second.

These conclusions are in harmony with the exceptions to regularity frequently observed in the lowest members of homologous series, and the general applicability of the rules has been tested by Lossen. Lossen finds that, so far as trustworthy data go, triads of oxygen compounds almost invariably conform to the rule; in the case of carbon compounds, however, although in most cases Dobriner's rule is obeyed, there are exceptions, notably in the case of the alcohols, where the boiling points have been often and carefully determined.

In triads containing the alkyl groups linked to sulphur, nitrogen, the halogens, and the metals, Lossen finds that in some cases the first difference is less, while in others it is greater, than the second difference.

As regards the boiling points of isomers, subsequent work has proved that in no case are the boiling points identical.

In 1868 Hinrichs stated that the more symmetrical the formula of an isomeric molecule is, the lower is the boiling point. Naumann extended this idea, and in 1874 put forward for paraffin derivatives the only rules which are capable of anything like general application. His conclusions are that:—The more nearly the grouping of the atoms in an isomeric molecule deviates from the rectilinear or chain type, and approaches the spherical type, the lower is the boiling point. In metameric bodies of similar chemical character and otherwise corresponding structure containing carbon, hydrogen, and oxygen, the more nearly the oxygen atom stands to the middle of the chain of atoms the lower is the boiling point. These two rules, applied singly or in conjunction, accord with the great majority of the facts. There are exceptions, however, among which some of the esters carefully examined by Gartenmeister may be noticed.

For isomers of aromatic series practically no generalisations have as yet been established.

Several attempts have been made to deduce formulæ whereby boiling points may be calculated. In the case of homologues, expressions such as those of Goldstein, Mills, and Hinrichs are no doubt successful in reproducing the observations for the particular series to which the formulæ refer, but they do not afford a basis for calculating boiling points in general.

Before entering upon an examination of Kopp's memoirs on specific volume, it may be interesting to give a brief history of the attempts made prior to his time to trace relations between chemical combination and the equivalent volumes of solid and liquid substances.*

* Objection has been raised to the term "specific volume" on the ground that as specific gravity is the weight of unit volume, specific volume should, by analogy, be the volume of unit weight—the reciprocal of specific gravity, and not the product of this reciprocal and molecular weight. Hence, of late years, the term

These attempts may be said to have grown out of Gay Lussac's memorable discovery in 1808, that gaseous bodies combine together in simple volumetric proportions. The first endeavour to apply similar considerations to solids and liquids was made in 1821 by "Le Royer, Pharmacien, and J. A. Dumas, son élève," the latter of whom is none other than our eminent Foreign Fellow, and the first of our Faraday Lecturers, the late perpetual Secretary of the French Academy. In their paper in the *Journal de Physique*, **92**, 408, Le Royer and Dumas attempted to determine the equivalent volumes of the elements by dividing their atomic weights by their respective specific gravities, the values so obtained being termed by them *atomic volumes*. They were led to conclude that these volumes formed an arithmetical series, a supposition which, it must be admitted, was hardly warranted by the facts then known, and which has since been completely disproved by more accurate observation. This idea of combination among solids in definite volumetric proportion was further developed in 1824 by W. Herapath in a paper read before the Bristol Society of Inquirers (*Phil. Mag.*, Nov., 1824), in which it was sought to prove that the volume of the oxygen in a metallic oxide bears a simple ratio to that of the metal with which it is combined. Almost simultaneously the same problem was attacked by Karsten (*Schweigg. Journal*, **65**, 394), and subsequently, in 1830, by Boullay, but with no definite theoretical result. Ammermüller, however, in 1840, was led to conclude (*Pogg. Ann.*, **49**, 341; *id.*, **50**, 406) that the specific volumes of compounds containing the same elements in different proportions are either identical or stand to one another in rational proportions. Persoz, in his *Introduction to the Study of Molecular Chemistry*, recognised that equivalent amounts of many bodies of analogous composition occupy the same volume, and he

"molecular" volume has been more generally preferred. It is, however, questionable whether the change is worth making, in view of the confusion which is almost certain to occur from the varying sense in which the term will be used by physicists and chemists. The real molecular volume is obviously the mass of a molecule divided by its density. Although such values are not yet known with any degree of precision, it can hardly be doubted that we are within measurable distance of this knowledge. The term specific volume is certainly not free from objection, but inasmuch as it has acquired, by definition, a distinctive meaning, no difficulty need be apprehended from its continued use.

Specific gravity referred to water at 4° is the weight in grams of the unit volume. If, then, the molecular weight be expressed in grams, we may define specific volume as the number of cubic centimetres occupied by this weight. The molecular weights here used refer to the gaseous state: the objection which has been urged against the employment of such weights has, however, lost much of its force now that the conception of the continuity of the gaseous and liquid states is generally accepted.

inferred that the specific volumes of all substances are multiples of one and the same number, a conclusion also drawn by Le Royer and Dumas, but which is not supported by facts.

Kopp's first memoir on the subject of specific volume appeared in *Poggendorff's Annalen* for 1839 under the title "Ueber die Vorausbestimmung des specifischen Gewichts einiger Klassen chemischer Verbindungen" (*Pogg. Ann.*, **47**, 133). In this paper he discusses the specific gravities of a number of compounds of metals and non-metals, and by means of certain assumptions, he deduces general formulæ from which he is able to calculate the specific gravities of certain oxides and haloïd salts with results which show, in general, a fair agreement with the observed values. In the same manner he calculates formulæ for other anhydrous salts, such as sulphates, carbonates, and nitrates, on the supposition that such salts consist of combinations of oxides and acids, or that they are made up of a radicle, acid, *plus* oxygen. By means of these formulæ he infers that it is possible to draw conclusions concerning the specific gravity of metals for which this constant is unknown. Kopp here uses the term *specific volume* for the first time, and he defines it as the molecular weight (*Mischungsgewicht*) of a body divided by its specific gravity. He finds that the specific volumes of similarly reactive elements, as, for example, chlorine, bromine, and iodine; tungsten, molybdenum, chromium, iron, manganese, nickel, cobalt, &c., are respectively equal or nearly equal. In other cases, as silver and gold, potassium and sodium, the specific volumes stand to each other in simple relations. Elements which, like barium and strontium, form isomorphous compounds show identity in specific volume, and Kopp sees in this fact an argument for the validity of the theory of hydrogen-acids; for, if we conceive that baryta replaces the strontia in an isomorphous strontium salt, it follows that the baryta will occupy a wholly different volume from the strontia; whereas, if barium replaces strontium in equivalent proportions, then since each element occupies practically the same volume, there is no *a priori* reason for any sensible change in crystalline form, which is in accordance with observation.

The conception of specific volume is still further expanded in a lecture given by Kopp to the Chemical Section of the "Naturforscher Versammlung"—the equivalent of our British Association for the Advancement of Science—at Erlangen, in 1840 (*Annalen*, **36**, 1 (1840)). He first attempts to prove that the specific weight of isomorphous substances is proportional to their atomic weight; or that isomorphous bodies possess the same atomic volume. Strictly speaking, this law can hold only for those substances which are perfectly isomorphous. The bodies termed isomorphous are, in general, only approximately so, for we find the angles of their crystals deviating several degrees from

one another; and the relations between the axes of bodies thus denominated isomorphous are not perfectly equal. The more nearly the crystalline forms of isomorphous substances are identical, the more nearly will their atomic volumes be the same. This is made evident by a comparison of the axial ratios of witherite, strontianite, arragonite, and cerussite; and also of the carbonates of zinc and magnesium, mesitene, the carbonates of iron and manganese, and dolomite and calcspar. It is seen that there is a direct comparison in the case of the latter compounds between the length of the principal axis a and the atomic volume V, such that $a^{4\cdot7\cdot9} = 0{\cdot}0127671\,V$, from which it is possible, of course, to deduce the specific gravity of the substance from its crystalline form. It also follows that an increase of atomic volume is occasioned by an increase in the length of the axis a. If, we heat one of these crystals, the density decreases, the axis a must therefore increase in length, whilst the angle R becomes less obtuse. This fact indeed, was discovered by Mitscherlich, who found that the specific gravity of calcspar decreased in the ratio of 1 to $\frac{1}{1{\cdot}001961}$ on being heated through 100°. The specific gravity of calcspar is 2·7220, when $a = 0{\cdot}8544$ and $R = 105°\ 5'$. By heating it through 100°, the sp. gr. becomes 2·7167, or its atomic volume changes from 36·73 to 36·80. If we determine the length of the axis a by means of the above formula, we find it 0·85672, corresponding to an angle R of 104° 57′, or a difference of 8′, which closely agrees with that actually observed by Mitscherlich (*Phil. Mag.* [3], **18**, 255).

Kopp's memoir, which gave to the specific gravity of a solid and liquid substance a new and important significance, attracted much attention and occasioned no little controversy. Schröder (*Pogg. Ann.*, 553 (1840)), starting from the observation of Ammermüller, that equal volumes of the two oxides of copper contain the same amounts of copper and multiple amounts of oxygen, assumed that the volume of the copper, as of the oxygen, is equal in the two substances, but that the amount of the oxygen in the cuprous oxide stands to that in the cupric oxide as 1 to 2. Hence Schröder drew the general conclusion that the same element can have different specific volumes in different compounds, but that the several values for the specific volumes stand in simple relations to each other. He saw in this hypothesis not only an explanation of the condensation which accompanies chemical union, but also a rational basis for the belief that the volume of a compound is equal to the sum of the volumes of its components.

Schröder's ideas, to begin with, had something in common with those of Kopp, but they underwent frequent modifications during the next 30 years. The characteristic manner in which the two philosophers presented their views was thus sketched by Berzelius:—

"Schröder is invariably of opinion that he has discovered what is right: to his thinking, the proofs he cites are evident; he is always convinced and insists that his reader is equally so . . . Kopp, on the other hand, draws attention not only to that which supports a statement but also to that which is adverse to it . . . He searches for truth, but he indicates, without reserve, what he provisionally regards as only probable."—(Quoted by Ostwald, *Stöchiometrie*, p. 620.)

Kopp's conceptions on the subject at this time took more formal shape in the small book he published in 1841, at Frankfort, *On the Specific Gravity of Chemical Compounds*. A summary of this work appeared in the *Phil. Mag.* for 1842, from which the following abstract is made:—Kopp points out that Schröder's contentions are weakened by the great number of arbitrary assumptions on which they are based. Schröder, in fact, would seem to forget that the probability of a theory becomes less in proportion as the number of assumptions on which it is founded becomes greater. Kopp believed that the state of knowledge at that time did not enable a perfect and consistent theory to be framed; all he asserted was, that one may be proposed of which a measure of its probability may be inferred from the fact that it explains the greatest number of experimental facts by the fewest possible assumptions. The atomic volume of a compound is seldom equal to the sum of the atomic volumes of its elements, that is, the "primitive atomic volumes" calculated from the specific gravity of the elements in the isolated state. If the atomic volume of a compound is greater than the primitive atomic volumes of either of its components, it is impossible, *a priori*, to say whether one or both of the elements are contained in it with an atomic volume different from the primitive value; but it is certain that one element in a compound does not possess its primitive atomic volume if the atomic volume of the compound is smaller than the primitive atomic volume of that element. It is not as yet possible to state for every compound which element enters into it with its primitive atomic volume, or whether both acquire different ones. It is only possible to infer this with any degree of probability in the case of analogous compounds which have *one* element in common.

Schröder found that if in a series of analogous bodies, AO, BO, CO, of which the specific volumes are known, we subtract from these values the primitive atomic volumes of A, B, and C respectively, we obtain a constant remainder. This he found to be the case with the oxides of lead, cadmium, and zinc, and hence he inferred that the metal in these oxides retains its primitive atomic volume. Kopp assumes that this is equally true of the salts of the heavy metals, but with the salts of the metals of the alkalis and alkaline earths, this

is impossible, as the specific volumes of the salts are, as a rule, smaller than the primitive atomic volumes of the component metals. He has consequently to assume for these metals a specific atomic volume which however remains the same in all the salts. He determines these values as follows:—Suppose M + R to be a compound of a heavy metal, m + R the analogous compound of a light one; suppose A to be the known specific volume of M + R, and a that of m + R, B the primitive atomic volume of M, and b that of m.

$$\text{Then, } M + R = A,$$
$$\text{and} \qquad M = B.$$

Therefore the atomic volume with which R is contained in the compound is A − B, say x.

It is assumed that R retains its value in m + R,

$$\text{and since } m + R = a,$$
$$\text{and} \qquad R = x;$$

therefore atomic volume of m (or b) $= a - x$. The specific volume of CO_2 in the carbonates is assumed to be 24·2, whence we have—

	Mol. vol. calc.	Sp. gr. calc.	Sp. gr. obs.
$PbCO_3$	42·4	6·30	6·43 to 6·47
$CdCO_3$.....	38·1	4·52	4·42 „ 4·49
$FeCO_3$	31·4	3·70	3·83 „ 3·87
$MnCO_3$.....	31·9	3·61	3·55 „ 3·59
Ag_2CO_3	44·8	6·15	6·08
$ZnCO_3$.....	33·6	3·72	4·34 to 4·45

With the exception of $ZnCO_3$, the observed and calculated specific gravities are fairly concordant.

By means of the values for the alkalis and alkaline earths, obtained as described, Kopp deduces the following specific volumes and specific gravities:—

	Mol. vol. calc.	Sp. gr. calc.	Sp. gr. obs.
$BaCO_3$.....	47·1	4·19	4·24 to 4·30
$CaCO_3$.....	33·8	2·96	2·70 „ ·300
K_2CO_3.....	61·6	2·25	2·26
$MgCO_3$	30·6	2·75	2·61
Na_2CO_3.....	45·0	2·36	2·47
$SrCO_3$.....	41·5	3·56	3·60 to 3·62

The specific volume of NO_3 is, in like manner, found to be 28·6.

	Mol. vol. calc.	Sp. gr. calc.	Sp. gr. obs.
$Pb(NO_3)_2$	75·5	4·40	4·40
$AgNO_3$	78·1	4·36	4·36
NH_4NO_3	92·1	1·74	1·74
$Ba(NO_3)_2$	80·1	3·20	3·19
KNO_3	94·7	2·14	2·10
$NaNO_3$	78·1	2·19	2·19
$Sr(NO_3)_2$	77·6	2·84	2·89

In certain of the sulphates, the value of the group SO_4 appears to be 37·8.

	Sp. gr. calc.	Sp. gr. obs.
$CuSO_4$	3·56	3·57
Ag_2SO_4	5·34	5·34
$ZnSO_4$	3·42	3·40
$CaSO_4$	2·90	2·93
$MgSO_4$	2·75	2·61
Na_2SO_4	2·44	2·46

In other sulphates, however, the group SO_4 appears to have the value 29·8.

	Sp. gr. calc.	Sp. gr. obs.
$PbSO_4$	6·32	6·30
$BaSO_4$	4·43	4·45
K_2SO_4	2·60	2·62
$SrSO_4$	3·90	3·95

In the chromates, $CrO_4 = 36·5$; and in the tungstates, $WO_4 = 39·0$.

	Calc. sp. gr.	Sp. gr. obs.
$PbCrO_4$	5·98	5·95
K_2CrO_4	2·69	2·64
$PbWO_4$	8·04	8·00
$FeWO_4$	6·67	7·10
$CaWO_4$	6·05	6·04

Cl, like SO_4, appears to have two distinct values, viz., 15·7 and 19·8.

	Sp. gr. calc.	Sp. gr. obs.
$PbCl_2$	5·60	5·68
$AgCl$	5·50	5·50
$BaCl_2$	3·83	3·86
$NaCl$	2·25	2·26
NH_4Cl	1·44	1·45
$CaCl_2$	2·29	2·27
KCl	1·94	1·94
$CuCl_2$	3·70	3·68
Hg_2Cl_2	6·90	6·99
$HgCl_2$	5·05	5·14
$SrCl_2$	2·80	2·80

The density of many oxides may be calculated on the assumption that the specific volume of O = 5·1.

	Sp. gr. calc.	Sp. gr. obs.
PbO	9·55	9·50
CdO	7·05	6·95
CuO	6·53	6·43
MnO	5·87	4·73
HgO	10·9	11·00
ZnO	5·48	5·43
SnO	6·28	6·67
MoO_2	6·01	5·67
TiO_2	4·16	4·18
PbO_2	8·40	8·90
Sb_2O_3	5·69	5·78
Pb_2O_3	8·91	8·94
Fe_2O_3	5·31	5·25
Co_2O_3	5·64	5·69
Fe, Ti } O_3	4·78	4·78
Bi_2O_3	8·09	8·17

The agreement, with the exception of the cases of MnO, SnO, MoO_2, and PbO_2, is fairly good.

In other oxides, O = 2·55, and in a third group 10·2, all the values, it will be observed, being multiples of a common number.

	Sp. gr. calc.	Sp. gr. obs.
SbO_2	6·53	6·53
SnO_2	7·03	6·96
Cr_2O_3	5·39	5·21
Cu_2O	5·87	5·75
Hg_2O	10·5	10·69
Ag_2O	7·48	7·25
MoO_3	3·44	3·46
WO_3	5·68	5·27

The specific gravity of a large number of the sulphides may, in like manner, be calculated, with a similar degree of approximation to the observed values, by assuming that sulphur, like its analogue, oxygen, has three values, viz., 8·5, 15·0, and 17·6.

Kopp also showed that the densities of the hydrated oxides, and of a number of hydrated salts, may be calculated with considerable accuracy by assuming certain definite values for water in a state of combination. It ought to be stated, however, in this connection, that

subsequent researches have indicated that Kopp's conclusions respecting the specific volume of water of crystallisation must be slightly modified. Schiff, many years ago, showed that the members of certain classes of hydrated salts have practically the same specific volume. Thus, all the alums have a specific volume of about 277; double sulphates of the form $M_2M''(SO_4)_2,6H_2O$ have a common volume of 207; and all the vitriols, that is, salts of the form $M''SO_4,7H_2O$, whether isomorphous or not, have the specific volume 146.

Lord Playfair sought, many years ago, to determine the precise relation of the specific volume of a salt to its degree of hydration. This work, the natural sequence of the memorable investigations which we owe to Playfair and Joule, was first made known through the medium of a paper communicated to this Society by your lecturer and Mr. John I. Watts ("On the Specific Volume of Water of Crystallisation," Trans., **37**, 102 (1880)). On learning that we were engaged on this question, Lord Playfair placed the very ample notes of the investigation which he was not able to complete, at our disposal, and although, at his suggestion, we went over the whole of the ground again, much of the experimental matter of our communication was based upon his previous observations. The main result of the enquiry was to show that the volume occupied by the several molecules of water varies with the degree of hydration of the salt. In the case of the so-called magnesian sulphates, the first molecule of water, the constitutional water, or "water of halhydration," of Graham, occupies considerably less bulk than the remaining molecules; its mean relative value is 10·7. Each additional molecule appears to occupy a gradually increasing volume. The difference between the monohydrate and dihydrate is 13·3; between the dihydrate and trihydrate it is 14·5; between the trihydrate and the tetrahydrate it is 15·4; and between the hexhydrate and heptahydrate it is 16·2. These observations are so far in harmony with Kopp's general conclusions that in the substances containing only a small number of water molecules (1 to 3) the specific volume of the water is 12·4; in others containing a larger number (2 to 7) it is 13·4; whereas, in a third class, containing the largest number (from 3 to 10), its mean value is 15·3. It need hardly be pointed out that the main conclusion agrees with general experience. Chemical combination results, as a rule, in contraction, and the stability of the compound is connected with the degree of this contraction. Now, it is well known that the different molecules of water in a hydrated salt are held with varying degrees of tenacity, as shown by the different amounts of heat required to expel them, and the different amounts, too, which are evolved in the rehydration of the salt.

Kopp finally seeks to disprove the assumption of Schröder that the

specific volume with which an element is contained in a compound bears a simple relation ($\frac{1}{2}$, $\frac{1}{3}-\frac{1}{9}$; $\frac{2}{1}$, $\frac{2}{3}-\frac{2}{9}$; $\frac{3}{1}$, $\frac{3}{2}-\frac{3}{9}$) to its primitive specific volume, an assumption which plays a not inconsiderable part in Schröder's subsequent papers, and in those of Hermann (*J. pr. Chem.*, **13**. 28 (1876)) and E Wilson (*Proc. Roy. Soc.*, **32**, 457).

Kopp had hitherto mainly concerned himself with the study of inorganic compounds, and for the most part with solid substances. He next turned to the consideration of organic bodies, and, in his papers of 1842, on the "Vorausbestimmung einiger physikalischen Eigenschaften bei mehreren Reihen organischer Verbindungen" (*Annalen*, **41**, 79; *ibid.*, **41**, 169), we have the first of a series of memoirs, on which his position as an observer will ultimately rest. For his purpose, the study of organic compounds presented many features of importance. In the first place, the variety of elements which enter into the composition of organic compounds is much smaller than in inorganic substances; and in the second, there are more liquid substances and a wider range in the mode of combination among the compounds of carbon than of any other element. These liquids, too, may, for the most part, be easily obtained of a sufficient degree of purity; they are readily characterised, and the determination of their specific gravity can be made with a higher degree of precision than in the case of solids. On the other hand, liquids are more expansible by heat than solids, and the question of the conditions under which specific volumes are comparable becomes of much greater importance in the one case than in the other. The main conclusion of this paper may be stated as follows:—If we imagine a number of analogous organic compounds arranged under the following scheme:—

A + α	B + α	C + α	D + α, ...
A + β	B + β	C + β	D + β, ...
A + γ	B + γ	C + γ	D + γ, ...
A + δ	B + δ	C + δ	D + δ, ...
....	....	....	....
....	....	....	....

where A, B, C, D, α, β, γ, δ are certain bodies or combinations of elements, then *it is only necessary to become acquainted with one horizontal and one vertical series to know the most important physical properties of all the combinations contained in such a table. If the properties of the compounds contained in one horizontal or in one vertical series are known, the mere knowledge of one of these compounds is sufficient in order to ascertain the properties of all the compounds arranged in any other horizontal or vertical series.*

If the specific volumes and the boiling points of the compound

A + α, A + β, A + γ, &c., are known, and we also know the specific gravity and boiling point of B + α, we can at once ascertain the specific gravities and boiling points of the bodies B + β, B + γ, B + δ. For between the specific volumes and boiling points of

A + α and B + α	B + α and D + α	A + α and A + δ,
A + β and B + β	B + β and D + β	B + α and B + δ,
A + γ and B + γ	B + γ and D + γ	C + δ and C + δ,
&c.	&c.	&c.,

the differences are the same.

A similar regularity occurs in the physical properties in cases of substitution, as, for example, that of chlorine for hydrogen. Let A represent a combination of oxygen and carbon which remains unaltered, α hydrogen, β chlorine, m, n, x, y numbers; we have then—

$$\begin{aligned} &A + m\alpha \quad\quad + n\beta, \\ &A + (m - x)\alpha + (n + x)\beta, \\ &A + (m - y)\alpha + (n + y)\beta. \end{aligned}$$

The sum of the atoms α and β remains the same in each compound. If in any compound x atoms of hydrogen are replaced by x atoms of chlorine, the specific volume of the new compound is increased by x . 12·5 (approximately).

The numerical basis upon which these generalisations rest was undoubtedly affected by the fact that Kopp at this period was unable to determine the precise conditions under which the comparisons of specific volume are valid; indeed, he is disposed to recognise in this circumstance the chief ground for the differences between the observed and theoretical values. But, in reality, the nature of the experimental material itself was hardly sufficient to afford absolute proof that Kopp's laws were capable of the mathematical precision with which he stated them. This fact was, indeed, recognised by Liebig in a note which he appended to Kopp's paper in the *Annalen*, and in which he called upon his fellow-workers to give increased attention to the ascertainment of those physical constants which serve to distinguish a chemical compound. Kopp's generalisations were undoubtedly first approximations to the expression of physical truths, but the limits of their application could only be determined by fuller and more accurate data, and by a clearer conception of the conditions under which the comparisons should be made.

In Kopp's next memoir, "Ueber den Zusammenhang zwischen der chemischen Constitution und einigen physikalischen Eigenschaften bei flussigen Verbindungen" (*Annalen*, **50**, 71, 1844), this last problem is more particularly attacked. The specific volumes of liquids are obviously dependent on heat; hence they may be said to

be comparable at temperatures at which heat exercises the same effect upon the liquids, say at their boiling points, or, in general, at temperatures at which their vapour pressures are equal. Fifty years ago, however, the vapour pressures of but three liquids were known, and these only with approximate accuracy, viz., water, alcohol, and ether, and hence, since Kopp assumed that the specific volume of alcohol was the sum of the specific volumes of water and ether, there were only two equations possible to determine the three unknown values of C, H, and O at all temperatures below the boiling points. On the assumption—which observation showed to be probable—that one atom of oxygen can replace two atoms of hydrogen in a compound without sensible alteration in specific volume, that the comparison may be made at equal distances of temperature from the boiling point instead of at the temperature of equal vapour pressures, and that the elements in combination have the same inherent expansibility, or, in other words, that the relation between the specific volumes of (C), (O), and (H) in a compound is the same at all distances from the boiling point, Kopp was able to deduce values for C, H, and O which enabled the specific gravity of a liquid consisting of these elements to be calculated at any temperature below its boiling point with a certain approximation to accuracy. He found that the specific volume of a liquid compound, consisting of (*a*) atoms of carbon; (*b*) atoms of hydrogen; (*c*) atoms of oxygen; (*d*) atoms of chlorine; (*e*) atoms of nitrogen; and (*f*) atoms of sulphur, is, for a temperature distant D° from its boiling point, approximately expressed by

$$(1{\cdot}28a + 0{\cdot}48b + 0{\cdot}96c + 2{\cdot}34d + 1{\cdot}44e + 2{\cdot}4f) \times (9{\cdot}75 - 0{\cdot}01\mathrm{D})^{*}.$$

Kopp warns his reader that this formula has no other value than as expressing the specific volume, and, indirectly, the specific gravity, of a liquid consisting of the above-named elements, with, on the whole, a fair degree of accuracy. He is careful to point out that it rests on assumptions for which definite experimental evidence is, in great measure, wanting. If both the form of the formula and the values of its constants were accurate, it would be possible to infer the boiling point of a liquid from a knowledge of its composition and its specific gravity. It would also follow, from the nature of the formula, that the contraction which a liquid experiences on cooling through X° from its boiling point was invariably proportional to X; whereas observation shows that the contraction for a given temperature interval becomes smaller and smaller as the distance from the

* The values were originally calculated on the basis of Berzelius' atomic weights; they have been transformed to the corresponding values when H = 1.

boiling point increases. Moreover, it assumes that two liquids, having the same volume at the boiling point, must necessarily possess the same volume at D° from the boiling point, which is also contrary to experience.

Kopp ventured to conclude, then, that in all probability—

1. Equal differences in composition corresponded with equal differences in specific volume.
2. Equivalent amounts of oxygen and hydrogen in liquid compounds occupy nearly the same volume.
3. The specific volume of a compound is equal to the sum of the specific volumes of its components. The same element almost invariably preserves the same specific volume. Isomeric compounds have the same specific volume; polymeric compounds have specific volumes which stand to one another in the same relation as the molecular weights of the compounds. Variations in the chemical constitution of isomeric compounds are without effect on their specific volume.
4. Comparisons of specific volumes of liquids are only valid at temperatures at which the vapour pressures of the liquids are equal.

These conclusions, as Kopp clearly recognised, rested on no very firm experimental basis; the necessary data, indeed, were not to hand to test them rigorously. Accordingly, he resolved to make accurate determinations of all the physical constants needed to ascertain, with the highest possible precision, the specific volumes of a large number of liquids.

In 1855, Kopp published the first of the series of memoirs in which he gave the results of his 10 years' experimental labours. These memoirs are, without doubt, the most remarkable and most characteristic of his scientific papers. They exhibit in a striking degree all the attributes of a successful investigator—ingenuity, manipulative skill, a rigid sense of accuracy, illimitable patience, insight, and inductive power.

His main conclusions may thus be summarised :—

1. The selection of the temperature of equal vapour tension as a basis of comparison seemed to be warranted by the fact that regularities are thereby made evident which otherwise are not apparent.
2. Differences of specific volume are proportional to differences in chemical composition.
3. Isomeric liquids of the same chemical type have equal specific volumes.

4. The substitution of hydrogen for an equivalent amount of oxygen only slightly affects the specific volume.
5. One atom of carbon can replace two atoms of hydrogen without alteration in specific volume.

It was further shown that the specific volume of a liquid was determined, not only by its composition, but also by its constitution. Kopp found, for example, that the relative position of the oxygen atom in a molecule affected its specific volume; carbonyl-oxygen and hydroxyl-oxygen have two very different values. Sulphur, in like manner, would appear to have two specific volumes, depending upon its position or mode of combination in a molecule.

Definite values for the specific volumes of carbon, hydrogen, and oxygen were obtained from the following considerations:—An increment of CH_2 corresponds to an increase of specific volume of 22. Since C and H_2 occupy the same volume, we have C = 11 and H = 5·5. The replacement of H_2 by carbonyl O is attended by a slight increase in the specific volume. Kopp found that the most probable value for this form of oxygen was 12·2. For hydroxyl-oxygen it is 7·8, obtained by subtracting the value for H_2 (11) from the specific volume of water, 18·8. Hence the specific volume of a compound $C_aH_bO_cO'_d$, where O is carbonyl-oxygen and O′ hydroxyl-oxygen, may be expressed by the formula

$$V = 11{\cdot}0a + 5{\cdot}5b + 12{\cdot}2c + 7{\cdot}8d,$$

which gives results in no case varying more than 4 per cent. from the observed value, and, in the great majority of cases, much less.

Determinate values for the halogens, and, with less precision, for phosphorus, arsenic, and antimony; silicon, titanium, and tin, were also obtained. As regards nitrogen, it was found that in the amines N = 2·3. The group CN = 28; that of NO_2 = 33. If, then, carbon and oxygen preserved their ordinary values in these radicles, N must possess at least three different values depending on the mode of combination. There is, however, no evidence to disprove the supposition that the values for the carbon and oxygen atoms are not equally affected in these groups. This, indeed, suggests the possibility that compound radicles like CO, HO, NO_2, CN, &c., may possess definite specific volumes which are not necessarily the sum of the specific volumes of the component atoms as ordinarily ascertained.

It remains to indicate how far these conclusions have stood the test of criticism and subsequent research, especially when viewed from the standpoint of modern dynamics and in the light of our present conceptions concerning constitution. In 1865, H. L. Buff (*Annalen*, **4** (Suppl.), 129) sought to show that the specific volume of carbon,

like that of oxygen and sulphur, is affected by its mode of combination; or, in other words, that carbon in unsaturated compounds has a greater specific volume than in saturated bodies; from which he surmised that the specific volume of an element is in general determined by its particular atomic value. With this exception, the subject received, practically, no further experimental treatment until about 1880, when a number of papers followed each other in rapid succession. Only the briefest possible summary is here possible. It was found that isomeric liquids have not invariably the same specific volume. Between ethylene and ethidene chlorides, for example, there is a greater difference than 4 per cent.; indeed, ethylene compounds in general appear to have smaller volumes than those calculated by Kopp's values. Städel further showed that in the series of the chlorinated and brominated ethanes and ethylenes, the isomer of higher boiling point, *i.e.*, the ethylene derivative, has invariably the lower specific volume. Since these compounds are all saturated and the only variable constituent is a monovalent element (Cl or Br), it would appear probable that the specific volume of the halogen is also variable. Isomeric hydrocarbons manifest similar differences, whence it is obvious that either one or both of the elements must have a slightly variable volume, depending on grouping or mode of combination; it may be that the iso-group, like the groups carbonyl, hydroxyl, nitryl, &c., has a special volume, which is not necessarily the sum of the volumes of the component atoms as deduced from Kopp's values. Kopp himself found that the volumes of isomers were, in a number of cases, only approximately equal, and in others quite unequal. The term "chemical type," used in the sense in which Gerhardt employs it, is not sufficiently distinctive to denote the differences, say, between the normal and iso-compounds, or, between aniline and picoline, and it is questionable whether Kopp would have considered such cases as coming within his rule.

The observed specific volumes of the aromatic compounds, also, are frequently lower than the calculated values. Indeed, our views as to the constitution of the aromatic compounds would lead us to expect that the specific volume of benzene (and the derivatives in which the benzene group functions) would probably be different from that deduced from observations made, for the most part, on compounds of totally different constitution. Kopp (*Annalen* (Suppl.), 5, 303 (1867)) showed from Louguinine's observations that whilst benzene has an abnormally low specific volume, its homologues show the constant increase of 22 for an increment of CH_2, which is what might be anticipated, since these bodies are produced by the addition (substitution) of methyl, ethyl, &c., to the benzene group. Jungfleisch's

observations on the specific volumes of the chlorine substitution products of benzene also seem to show that the positions of the chlorine atoms affect, in a very marked manner, the specific volume of the product (*Compt. rend.*, **64**, 911). Further observation has shown that Kopp's conclusion, that liquid elements and radicles have the same volume in combination as in the free state, is well founded. Thus the observed volume of NO_2 = 32·0, calculated, 31·5; observed volume of Br = 53·6, calculated, 53·4; observed volume of CN = 28·9, calculated, 28·9. The observed specific volume of Cl from Knietsch's careful determinations of the specific gravity of liquid chlorine is 22·8; the mean calculated value is 22·7. Kopp surmised that members of the same chemical family would be found to have the same specific volume; observation shows, however, that the specific volumes gradually increase with the increase of atomic mass.*

Thanks to Roberto Schiff, Lothar Meyer, and his pupils, and especially to Lossen and his pupils, a very large amount of experimental material has been accumulated during the last ten years, from which important deductions may be drawn as to the general validity and limitations of Kopp's conclusions. Schiff (*Annalen*, **220**, 71 (1883)), by means of an improved form of an apparatus first suggested by Ramsay (Trans., 1879, **35**, 463), concluded that whilst it is generally true that isomeric compounds have slightly different specific volumes, it is almost invariably the case that the substance possessing the higher boiling point has also the higher specific volume (compare Städel). In the case of the metameric esters of the fatty acids, it is found that, as a rule, the specific volumes increase with the diminution of the number of carbon atoms in the acid radicle and with the increase in the alcohol radicle. At the same time, it would appear that the differences between the observed and calculated values are mainly due to the alcohol, the acid apparently having but slight influence. This is in conformity with Lossen's observations, that whilst the ethers and acids give experimental values which are almost in exact accordance with Kopp's values, the aldehydes and alcohols show wider variations, methyl alcohol giving too great an observed value, whilst the others give smaller and smaller values as the amount of carbon increases. It is, however, noteworthy that the differences between the aldehydes and derived alcohols remain almost constant, which is not the case with the aldehydes and acids, where it appears to increase with the molecular weight. Hence the differences between the homologous aldehydes are very nearly equal to those between the

* Thorpe: "On the Relation between the Molecular Weights of Substances and their Specific Gravities when in the Liquid State," Trans., 1880, **37**, 141; *ibid.*, 327.

corresponding homologous alcohols (Lossen). The mode in which carbon is combined in an organic compound has, according to Schiff, a distinct influence on its specific volume; like Buff, he finds that double-linked carbon occupies a smaller volume than when single-linked. It is, however, very doubtful whether the facts at present known are sufficient to establish this conclusion.

The examination of the very large quantity of experimental material which is now before us forces us to the conclusion that molecular volume is not a purely additive property. There is no longer room for doubt that the molecular volumes of substances are affected by far more conditions than we have hitherto taken cognisance of. The value $CH_2 = 22$ has no other significance than as expressing the average increment in volume in successive members of a homologous series. Indeed, as the physical data increase, it becomes doubtful whether even this mean value is correct. Later observations appear to show that the value augments as the series is ascended. The relation $C = 2H$ no longer applies to carbon compounds in general. What is true of carbon and hydrogen is equally true of oxygen, whether as carbonyl- or as hydroxyl-oxygen. No definite or uniform values can be assigned to oxygen such that the molecular volume of a liquid can be *a priori* determined. The values given by Kopp are simply mean values, but the actual volumes are affected by conditions of which, as yet, we have no very precise knowledge or any certain means of measuring. The values for the other elements are, of course, affected by these considerations. Thus the specific volume of chlorine is obtained on the assumption that the values for carbon and hydrogen are constant. All, then, tends to show that the molecular volume is not the sum of constant atomic volumes.

Lossen has attempted, and with considerable success, to devise formulæ which shall take note, or express the measure, of the influences which affect the uniformity in the values of specific volumes in organic compounds (*Annalen*, **254**, 42). These formulæ, as yet, can only be considered as first approximations, but their value will be evident from the fact that they serve to reproduce the observed values with a greater approach to accuracy than has hitherto been possible. Out of the 407 compounds which constituted the experimental material on which these formulæ are based, the observed molecular volumes of 352 differ by less than 2 per cent. from the calculated volumes. Comparatively few of these differences may be ascribed to experimental errors. In the main, they are caused by influences of structure and composition which, as yet, we have no certain means of measuring, such as the effect of substituted chlorine, or the special effect of the iso-group, or of the ortho-, meta-, or para-position, &c.

No summary of the present state of our knowledge respecting this

question would be complete without some reference to Schröder's later views. For nearly 50 years Schröder laboured unremittingly to throw light on the connection between volume and molecular weight, and the final form of his theory is too suggestive to be passed over in silence. Schröder regards the atomic volume of an element in combination as variable within limits determined by the nature of the chemical compound. In any one compound, however, all the elementary atoms occupy either equal or multiple volumes. Hence every molecular volume is a multiple of a certain *space-unit* or *stere*, the value of which may vary between 6·7 and 7·4, depending on the number, nature, and mode of union of the atoms. Ostwald, to whom I am indebted for this presentation of Schröder's argument, thus explains how Schröder obtains his determinate relations. The molecular volumes of formic, acetic, and propionic acids increase about 22 units for each increment of CH_2; in the case of alcohols the increase is about 20 units. The volume of formic acid is 41·8, that is, $2 \times 20{\cdot}9$; that of methyl alcohol is 42·7 or $2 \times 21{\cdot}4$. Hence it follows that in formic acid, CH_2O_2, the O_2 occupies the same volume as CH_2; and in methyl alcohol, CH_4O, the H_2O has the same volume as CH_2. In like manner, ethyl alcohol, C_2H_6O, has the volume 62·2, that is, $3 \times 20{\cdot}7$. Since $2 \times CH_2 = 2 \times 20{\cdot}7$, then $H_2O = 20{\cdot}7$. Acetic acid has the volume 63·5, that is, $3 \times 21{\cdot}2$; $2CH_2$ is $2 \times 21{\cdot}2$ and $O_2 = 21{\cdot}2$. The volume of acetaldehyde is 56·9, that is, about 6·6 smaller than that of acetic acid; this would indicate that the substitution of OH by H lowers the volume by 6·6. Since $H_2O = 21{\cdot}4$, it follows that the hydrogen and oxygen in hydroxyl each occupy one space unit or stere. As $CH_2 = 21$, we find that carbon also occupies one stere or space unit. Now from the volume of formic acid, which contains 6 steres, it is found on subtracting 3 steres for CH_2 and 1 stere for hydroxyl-oxygen, that the carbonyl-oxygen must occupy 2 steres.

We obtain then the following rule :—*The number of space units or steres of the saturated compounds of carbon, hydrogen, and oxygen corresponds to the number of the atoms, increased by as many units as there are atoms of carbonyl oxygen present.*

If we calculate, by means of this rule, the steres of the saturated compounds, we find that they vary within narrow limits and for the most part increase with increasing molecular weight. In the greater number of cases, the values range between 6·9 and 7·2. Ostwald has calculated the value of the stere for a large number of aliphatic compounds with the following results :—

Hydrocarbons, 6·89; 6·99; 6·82; 7·11; 7·23.
Alcohols, 7·12; 6·91; 6·77; 6·88; 6·78; 6·78; 6·81; 6·74; 7·09.

Acids, 6·97; 7·06; 7·11; 7·19; 7·24; 7·24; 6·85.
Esters, 7·04; 7·08; 7·05; 7·14; 7·26; 7·43; 7·45; 7·47.
Aldehydes, 7·11; 7·05; 7·18; 7·01; 7·18; 6·93; 7·27.

In the series of the hydrocarbons, the acids, and the esters, the steres, in the case of the normal compounds, increase regularly with increasing molecular weight; in that of the alcohols they decrease up to the third member and then increase. The secondary and tertiary compounds, have, as a rule, smaller steres than the normal compounds. It is instructive to note the different manner in which Kopp and Schröder arrived at the volume relations of these elements. Kopp concluded from the approximately equal volumes of the alcohols and corresponding acids, that H_2 and O are volumetrically equivalent; and from the equivalence of the volumes of benzyl and amyl compounds he inferred that C_2 and H_4 are mutually replaceable without alteration of volume; hence he assumed that the hydrogen atom occupies only half the volume of the oxygen or carbon atom. Schröder establishes the volume equivalence of CH_2, HOH, and O′O, and he inferred from the difference in volume between alcohol and aldehyde that hydroxyl oxygen has the same volume as hydrogen and carbon, whilst carbonyl oxygen has twice the volume. Whilst then Kopp assumes (approximately) $H_2 = C = O$, Schröder makes $H = C = O$.

In the case of unsaturated and aromatic compounds, Schröder assumes that each double linkage is attended with an increase of volume amounting to one stere; hence the foregoing rule has to be modified in this sense when applied to compounds of this class. The value of the stere in a number of unsaturated compounds is found to be—

Hydrocarbons, 6·87; 7·09; 6·93; 6·99.
Alcohols, 6·72.
Esters and ethers, 7·14; 7·13.

The values vary, practically, within the same limits as in the aliphatic compounds.

As regards aromatic compounds, it would seem to follow, from the identity in the volumes of benzoyl and amyl compounds, as indicated by Kopp, as well as from the corresponding relation between the isobutyl and phenyl compounds, that C_6H_5 comprises the same number of steres as C_4H_9, that is, 13. Of these, five are occupied by hydrogen; so that the carbon group C_6 occupies 8 steres.

The values of the stere in a number of aromatic compounds are as follows:—

Hydrocarbons, 6·85; 6·94; 6·98; 7·00; 6·95; 7·04; 7·04; 7·01; 7·06; 6·84.

Other compounds, 6·91; 6·87; 7·05; 6·97; 7·16; 7·26; 7·50; 7·28; 7·14; 6·96; 7·07.

The value of the stere here also varies within the usual limits; it is comparatively small for the hydrocarbons (6·8—7·0), larger in the case of the alcohols, and still larger in that of the esters (7·2—7·5). Those relations if substantiated would seem to indicate that the law of volumetric combination among the masses of liquid molecules is essentially not more complex than the law of combination between those of gaseous molecules.

There is one consideration which is vital to the whole question, and to which, therefore, a brief reference must be made. It relates to the choice of conditions under which the values we term molecular or specific volumes are really comparable. Although Horstmann and Lossen have advanced reasons against the practice, contending that at any other temperature, say 0°, relations similar to those now established are made manifest, it has been the custom, in accordance with Kopp's direction, to compare the specific volumes of liquids at the temperatures of their respective boiling points under a standard atmosphere. Whether, however, the temperature of the boiling point, under these circumstances, is a truly comparable condition is open to question. It has been urged by Horstmann that, since what we call atomic volume is the space not merely *filled* by an atom, but also that in which "it moves, and lives, and has its being," it is not *a priori* probable that at temperature which differs, say, by 300°, as, for example, in the case of C_4H_{10} (boiling point 1°) and $C_{18}H_{38}$ (boiling point 317°), these volumes will be the same. Moreover, as pointed out by Bartoli, the boiling point cannot, in the nature of things, be a strictly comparable condition, since it is affected by pressure to a different extent in the case of different liquids. Objections of even greater weight may be urged against the suggestions of Tschermak and Krafft, to take the melting point as a comparable state.

No doubt, theoretically speaking, a valid condition should be when pressure, volume, and temperature are expressed in terms of their critical values. But that certain regularities in the molecular volumes at the boiling points have, in spite of this, been discovered, may be explained, as Guldberg has shown, when we compare the values of T_1, the absolute boiling point, with those of T, the absolute critical temperature; in those cases in which these two constants are known, the ratio T/T_1 approximates to $\frac{3}{2}$. Hence it follows that qualities like molecular volumes, which alter only slowly with temperature, are comparable at the ordinary boiling points (*Zeits. für Physikal Chem.*, **5**, 374).

It ought, perhaps, to be stated that subsequent observations show that the so-called "corresponding temperatures" deduced from Van der Waals' generalisations have not that degree of validity as temperatures of comparison which they were originally assumed to possess. Indeed, the present condition of knowledge warrants the statement that Kopp's original method of comparison is as valuable as any yet indicated.

Kopp continued to the last to interest himself in the problem which had been the mainspring of his scientific activity. Shortly before his death, he gave to the world, through the *Annalen* (**250**, 1889, 1), a critical account, written with the dignity and calm that befits the well-earned leisure of a veteran controversialist, of the many strivings which had been made to solve it since the tentative efforts he put forth in his thesis of 1838.

We rise from the perusal of this memoir with the conviction that, after all, the work thus summarised takes us but little beyond the threshold of the fundamental truth of which its author was the first to perceive the indication.

As yet we see through a glass darkly, and know only in part; but with the fuller light of a rapidly advancing knowledge, we shall most certainly get an insight into the causes which affect the universality of Kopp's conclusions. The discrepancies, if we could only read them aright, contain within them the clues to a broader generalisation which will more clearly connect the chemical nature of molecules with their physical attributes. Our experimental material will soon be sufficient for the basis of this generalisation, even if it is not so already. What is wanted is another Kopp to interpret it correctly.

MARIGNAC MEMORIAL LECTURE.*

The Life-Work of Marignac.

By P. T. Cleve, Professor of Chemistry in the University of Upsala.

Jean Charles Galissard de Marignac, who was elected a Foreign Fellow of the Chemical Society on the 19th June, 1862, was descended from Pierre Galissard, Seigneur de Marignac in Languedoc, whose son of the same name was made a citizen of Geneva in 1733. The subject of this memoir was born on April 24th, 1817, at Geneva, where his father, Jacob de Marignac, was a judge and *Conseiller d'Etat*. His mother was the sister of Elie le Royer, whose well-known pharmacy occupied a portion of the house in which the Marignacs resided. This pharmacy is noteworthy in the history of science as the place where Dumas obtained his first instruction in practical chemistry. Le Royer enjoyed a considerable reputation as a chemist and physiologist, and his house in the Rues-Basses was the meeting place of Prevost, De Candolle, and other men of science who were settled in, or who visited, Geneva at that period. These circumstances had, no doubt, their influence in developing the young Marignac's inclination towards natural science, and his life-long friendship with the great French chemist, whom we had also the honour to number among our Foreign Members, dates from this time. At the age of 16, Marignac went to Paris as a student at the *Ecole Polytechnique*, from which he passed—1837 to 1839—to the *Ecole des Mines*. The greater part of the following year was spent in travel in Scandinavia, Denmark, and Germany, the young "élève-ingénieur des mines" being charged with the preparation of reports upon the machinery employed in these countries. The only published outcome of these travels is a description of Henschel's blowing engine in use at the foundry of Veckerhagen, which appears in the *Annales des Mines* for 1824. The notes and drawings which he made during his travels are still preserved, and his biographer, Professor Ador, upon whose charming sketch the present biographical notice is largely based, finds in a note relating to Brussels an indication of that love of solitude and retirement which characterised Marignac through life, in the remark: "Les boulevards qui conduisent au Jardin Botanique sont encore une plus jolie promenade que le parc, car on n'y rencontre personne."

At that epoch, Liebig's laboratory in Giessen was the Mecca towards which nearly every young aspirant for chemical fame directed

* Chemical Society's Memorial Lectures. No. IV.

his steps, and thither Marignac repaired during the winter of 1840, to occupy himself with the study of some derivatives of naphthalene and of phthalic acid; this was his first and last essay in organic chemistry. Prout's hypothesis became to him, as it did to Stas, the primary impulse of almost all his subsequent work; its influence indeed can be detected in nearly all his memoirs in spite of their range and diversity of subject.

Marignac left Germany to take up a post in succession to Malaguti in the famous porcelain manufactory at Sèvres, then under the direction of Alexandre Brongniart, the father-in-law of Dumas, to whose influence the young Genevese chemist doubtless owed his preferment. Although the prospects of the position were promising, Marignac's tastes predisposed him towards an academic career, and in less than half a year he returned to his native town to take up the Professorship of Chemistry in the Academy. "La paie offerte," says Ador, "était modeste, très modeste, la position modeste aussi." To this Chair he added that of Mineralogy in 1845, and he continued to occupy both up to 1878, when the condition of his health compelled him to resign. The laboratory in which he so zealously laboured for upwards of 30 years, and which was the birthplace of his most important investigations, is described as a damp and gloomy cellar, more like the den of an alchemist than the workroom of a modern chemist. Here he worked alone and without assistance. When, in 1873, the Academy grew into the University, Marignac came into possession of the fine laboratory of which Geneva now boasts; and much of his time was occupied in its construction and equipment. He remained here only five years, and on his resignation arranged for himself, on the upper floor of his house in the Rue Senebier, a laboratory, the installation of which was of the simplest nature, quite in harmony with the rare modesty which characterised its owner. He continued to work here until about the year 1884, when his growing infirmity forced him to renounce all scientific investigation. After ten weary years of physical prostration, during much of which he was able to move only from his bed to his armchair, but with a mind active and clear to the last, he was released by death on the 15th April, 1894.

The probity and exactitude of Marignac's work are known to every chemist. In spite of a love of retirement, which it must be admitted in some ways impaired his usefulness as an university teacher, Marignac could not escape the recognition which was extended to him by almost every learned body in Europe. As Cicero says, "magnum virum tamquam umbra gloria sequitur," proved to be true of Marignac. Most scientific societies counted it an honour to number him among their Fellows, and he received many distinctions, among

them the Davy Medal in 1886, and the Order "pour le Mérite," given to him in 1881 by the German Emperor.

Marignac's first important work in inorganic chemistry was made with a view to test Prout's hypothesis. He sought to determine as exactly as possible the atomic weights of chlorine, potassium, and silver, thus repeating the work of Berzelius, who says (*Lehrb.*, **3**, 1189) that, although he considered his own determinations were not lacking in accuracy, they were surpassed by those of Marignac, and that none before him had attained such a high degree of precision. The great Swedish chemist wrote to Marignac: "Je regrette de n'avoir point pu prévoir, lors de votre visite à Stockholm que celui que je présentais comme un ingénieur des mines devait sitôt commencer à occuper une place élevée dans la chimie." Afterwards Marignac redetermined the atomic weights of bromine, iodine, nitrogen, and carbon; in fact, stoichiometry occupied him to the last, and in the course of his life he determined the atomic weights of no fewer than 28 elements. These researches led him into almost every branch of inorganic chemistry; among these was that of the rare earths, the tantalum group, the fluoro-salts, the complex acids, &c., and in all he made discoveries of the highest significance.

Marignac's work on the rare earths is undoubtedly the most important in this particular department of chemistry. His first investigations were made as early as 1840, when he was barely 23 years of age. Following Mosander, he attacked the cerite earths with the principal object of determining the atomic weights of the elements. The results were published in 1848–49. In 1853, followed a research on didymium. After an interval of more than 20 years, he again returned to the subject of the rare earths—this time to the metals of the yttria group. In 1878, he succeeded in separating ytterbia out of what up to that time was regarded as pure erbia, and it was in examining his fractionations from erbia that Soret found the absorption bands of the metal X, now known to be holmium. In 1880, Marignac extended his researches to the samarskite earths, and succeeded in isolating two new oxides provisionally designated as $Y\alpha$ and $Y\beta$. These are now respectively known as gadolinia and samaria.

A rapid survey of the history of the rare earths will serve to more clearly define Marignac's relations to the development of this branch of chemistry.

In 1794, the Finnish chemist, Gadolin, discovered a new earth or oxide in a black mineral found at Ytterby, near Stockholm. This substance he called yttria. In 1803, another Scandinavian mineral, also known in the past century as "the heavy stone from Bastnäs," and now called cerite, was examined in Sweden by Berzelius and Hisinger,

and in Germany by Klaproth. It was found to contain a new oxide, which the Swedish chemists named ceria, after the newly-discovered planet Ceres: Klaproth termed it *ochroiterde*, on account of its yellow colour. Mosander, in 1839, showed that this earth contained another oxide, lanthana, which he subsequently, in 1842, resolved into two distinct oxides, one giving colourless salts, to which he reserved the name lanthana, the other giving pink salts, which he called didymia. At about the same time, Scherer observed that yttria becomes yellow if strongly heated in an open vessel, whereas it is white if heated in a closed crucible, from which he inferred that yttria, like the ceria of Berzelius, was probably a mixture. In the following year, 1843, Mosander proved that by the partial precipitation of yttria salts with ammonia and acid potassium oxalate, the so-called yttria could be resolved into three earths, one of which was white, and gave colourless salts, and for which the name yttria was reserved, the second giving rose-coloured salts, to which the name terbia was given, whilst the third, known as erbia, afforded colourless salts and a deep yellow peroxide. The yttria earths were re-examined in 1860 by Berlin, who, for the first time, employed the method of the partial decomposition of the anhydrous nitrates by fusion. He could only detect two earths in the yttria of Gadolin, namely, the yttria of Mosander, giving white salts, and an oxide, furnishing rose-coloured salts, to which he restricted the name erbia. Hence, according to Berlin, terbia had no existence. All subsequent workers followed Berlin in designating the rose-coloured earth as erbia.

Shortly after the discovery of the spectroscope, Gladstone, in 1858, observed the beautiful absorption spectrum of didymia, and Bahr, in 1862, detected that of erbia. Delafontaine extended the application of the spectroscope in the investigation of the rare earths, and demonstrated the existence in Gadolin's yttria of Mosander's third earth giving a yellow peroxide. Inasmuch, however, as the term erbia had now come to be applied to the rose-coloured oxide, Delafontaine, in resuscitating Mosander's name of terbia, applied it to that earth which had been originally called erbia. In 1866 appeared the work by Bahr and Bunsen, who used Berlin's method, but with the modification that the anhydrous nitrates were so heated that they furnished a residue which was still soluble in boiling water, so that, on cooling, basic nitrates crystallised out. In this manner they succeeded, like Berlin, in resolving Gadolin's yttria into the true or white yttria and rose-coloured erbia, and they further determined the atomic weights on the assumption that these oxides had the general formula RO. The same formula was also applied to the cerite oxides.

In 1871, Mendeléeff published his celebrated paper on the Periodic Law. In discussing the position of these elements in his system, it was necessary to change the formulæ, hitherto considered beyond doubt, of their oxides. For yttria, didymia, and the monoxide of cerium, he proposed the formula R_2O_3; and lanthana he considered to be a dioxide, RO_2. At that time, few facts were known to justify such a change, the compounds of the rare earth metals having been but slightly investigated. The examination of the composition of the yttrium and erbium compounds was the principal object of the researches of Cleve and Höglund, who, in 1873, repeated the work of Bahr and Bunsen. This work was followed, in 1874, by Cleve's new researches on yttria, erbia, didymia, and lanthana, and in 1875 by that of Jolin on the compounds of cerium. The composition of the salts demonstrated the correctness of the predictions of the Russian chemist, with the exception of that relating to lanthana, which was shown to be a sesquioxide. When Hillebrand and Norton in 1875 isolated the metals, their specific heats were found to be in accord with the new atomic weights, and hence with the triadicity of the elements.

In 1878, the chemistry of the rare earths entered upon a new phase; the mineral samarskite, found in large quantities in North America, became now the raw material for preparing them. Whilst it contains much less erbia than gadolinite, it furnishes considerably larger quantities of the yellow earth terbia, as recognised by Delafontaine, from the sparing solubility of its formate. In this mineral, Delafontaine inferred the existence of a new earth, which he named philippia, the formate of which was more soluble in water than the terbium salt. Its salts, which are colourless, are characterised by the absorption band l 450. Roscoe (*Chem. Soc. J.*, 1882, 277) subsequently proved that Delafontaine's philippia was a mixture of terbia and yttria. In reality, however, the absorption band belongs to an element now known as dysprosium. A second new metal, decipium, was found in samarskite by Delafontaine (*C. R.*, **87**, 632), who at that time characterised it by the absorption bands l 416 and l 478. Moreover the didymia prepared from samarskite was believed to contain unknown elements. It was subsequently found that the absorption bands l 416 and l 478 belonged to the element now called samarium. Hence samarium would have been more properly called decipium, had not Delafontaine, in 1881, declared that his decipia of 1878 could be resolved into an oxide without absorption spectrum, for which he retained the name decipia, and into a second with absorption bands for which he adopted the name samaria, given by Lecoq de Boisbaudran. At about this period, Lawrence Smith announced the existence in samarskite of a new metal, which he called mosandrum. Marignac (*C. R.*, **87**, 281) and Delafontaine (*C. R.*, **87**, 600) independently proved that Smith's

mosandrum was identical with terbium. Subsequently, Lecoq de Boisbaudran (*C. R.*, **102**, 647) showed that mosandria was a mixture of terbia and gadolinia.

Marignac sought to prepare terbia from gadolinite, and succeeded in obtaining an oxide of a deep orange colour, giving colourless salts without absorption spectrum (*Bibl. uni. Arch. sci. ph. nat.*, **61**, 283). The atomic weight of the element was found to be 148·5 (Te_2O_3), and much lower, therefore, than the atomic weight, 163·1, as determined in 1886, by Lecoq de Boisbaudran. In examining the erbia from gadolinite, Marignac in 1878 made the unexpected discovery that this earth contained a new oxide, which gives colourless salts without absorption bands (*loc. cit.*, **64**, 97). He called the metal of this oxide ytterbium, and assigned to it the atomic weight of 172·5. In the erbia fractions obtained by Marignac, Soret (*C. R.*, **86**, 1062) found absorption bands, which could not be attributed to erbium. He called the oxide producing these bands X. In the following year, 1879, Nilson repeated Marignac's work on ytterbium, and found its atomic weight half a unit higher, or 173; he also examined some of its compounds. Lecoq de Boisbaudran and Thalén described its spark spectra. The correctness of Marignac's work was thus substantiated. Nilson, however, found that ytterbia was accompanied by another earth having a lower molecular weight; with the aid of the spectroscopic researches of Thalén he succeeded in proving its individuality, and called the new element scandium. Cleve also examined Mosander's erbia, and found, with Thalén's aid, that the absorption bands hitherto assigned to erbia belonged to three different oxides, one of which, called holmia, was identical with Soret's X, the other, hitherto undetected, between erbia and ytterbia, was called thulia. Cleve also succeeded in extracting Nilson's scandia from gadolinite and from yttrotantalite, and proved that the element scandium corresponded with Mendeléeff's hypothetical *ekaboron*, a conclusion also verified in the following year, 1880, by Nilson.

Neither holmia nor thulia have hitherto been obtained free from the accompanying earths. In 1886, Lecoq de Boisbaudran found that holmia was a mixture of two earths, the true holmia and dysprosium (*C. R.*, **102**, 1003), characterised by several bands. Crookes, however, found that only one of these, *l* 451·5, belonged to dysprosia.

At about this time, Marignac turned his attention to the samarskite earths (*Bibl. uni. Arch. sc. ph. nat.*, 1880, 413). By fractionation of the double potassium sulphate salts, he isolated in an almost pure state two oxides, $Y\alpha$ and $Y\beta$; the former was white, and gave colourless salts without absorption bands, the latter gave yellow salts, distinguished by the spectrum of samarium. In the year 1886

(*C. R.*, **102**, 902), the metal in Yα was called gadolinium. It is without doubt a perfectly definite element, although, according to Lecoq de Boisbaudran, Marignac's oxide probably contained about 10 per cent. of foreign oxides (*C. R.*, **108**, 165). Its spark spectrum was examined by Lecoq de Boisbaudran (*C. R.*, **111**, 472). With a sample prepared as pure as possible by Cleve, no emission lines in the spark spectrum could be obtained by Thalén, nor was Bettendorff more successful. The atomic weight of gadolinium was found by Marignac to be 156·75; by Lecoq de Boisbaudran, 155·9; by Cleve, 155 (*C. R.*, **111**, 409); by Bettendorff, 156·33.

The identity of Yβ with the samarium of Lecoq de Boisbaudran, the original decipium of Delafontaine, cannot be doubted. Its individuality has, however, been questioned by Lecoq de Boisbaudran and Demarçay (*C. R.*, 1886, **111**, 1551). Recently (1893) Demarçay has declared that no facts proving the complex nature of samarium have been established (*C. R.*, **117**, 163); Bettendorff has also arrived at the same conclusion (*Annalen*, **256**, 159; **263**, 164). The atomic weight of samarium was found by Marignac to be 149·4; by Brauner, to be 150; by Cleve, as 150·02; by Bettendorff, 150·09.

In the year 1883, Crookes (*Roy. Soc. Proc.*, **35**, 76) made the important discovery that the basic sulphates of certain of the rare earths become phosphorescent when exposed in a vacuum tube to the electric discharge, and that the light so emitted affords characteristic spectra. Soon afterwards (1884) Lecoq de Boisbaudran (*C. R.*, **100**, 1437) discovered another method of obtaining phosphorescent spectra. If the positive pole be immersed in a solution, and the negative pole be brought just above its surface, the light which is emitted gives an inversion spectrum nearly related to that of Crookes. In some cases these spectra are extremely delicate. They are, however, greatly influenced by foreign substances, and in the case of the inversion spectrum of Lecoq de Boisbaudran the character of the spectrum depends upon whether the spark issues at the centre or at the margin of the solution. Moreover, the brilliancy of the bands is not related to the quantity of the active substance present; a mixture of a small quantity with an inert substance may produce a more brilliant spectrum than the pure substance.

Crookes subjected (impure) yttria to an extensive series of fractionations, and found that the bands of the original spectrum became distributed among the different fractions. He considered that yttria was thus split up into a number of components, or, as he termed them, "*meta-elements*," and, on the basis of this observation, he advanced his theory of the "genesis of the elements" (*Chem. Soc. J.*, 1889, 250). The main conclusion was vigorously combated by Lecoq de Boisbaudran, who assigned some of the bands to elements in no

wise related to yttria, Zα and Zβ, of which the former follows holmium, and the latter may be identical with terbium (*C. R.*, **102**, 1536; **103**, 627; *Bull. Soc. Chim.*, 3 (3rd ser.) 53). Perfectly pure yttria gives no phosphorescent spectrum.

It has been pointed out that from the didymia of Mosander Delafontaine extracted samarium. In the year 1885, another element, praseodymium, was separated from didymia by Auer von Welsbach (*Monatsh.*, **6**, 477). This substance is characterised by the green colour of its salts, by its dark brown peroxide, and by its absorption-emission spectrum; its atomic weight is 143·6. It is probable that didymia will still furnish new elements. Its spectrum contains a band, *l* 475, that cannot belong to didymia (Crookes, *C. R.*, 1886, **102**, 1551; Demarçay, *C. R.*, **104**, 580). Another band, *l* 462, according to Demarçay, probably belongs to the same element as that furnishing *l* 475, but Crookes believes it to belong to the samarium series. In the year 1886, Crookes stated that it was possible to eliminate band after band from the original didymium spectrum, so that only the band *l* 443 remained (*Roy. Soc. Proc.*, **40**, 563). Krüss and Nilson (*Ber.*, **20**, 2134, 3067; **21**, 585, 2019), and Kiesewetter and Krüss (*Ber.*, **21**, 2310), on examining the absorption spectra of earths extracted from various minerals, arrived in 1887 at a somewhat similar conclusion, not only as regards didymia, but also as regards all other earths with absorption spectra. Didymia, freed from samaria and praseo-dymia, is said, for example, to contain no fewer than nine elements. C. M. Thompson (*Chem. News*, **64**, 167; *Ber.*, 1891, *Rep.*, p. 975), however, finds that the absorption spectrum of didymium, extracted from various minerals, does not show any difference of importance. With respect to the conclusion of Krüss and Nilson, it must be remembered that the observations were made upon materials containing several oxides giving absorption bands, and it may happen that the intensity of certain bands of a particular element may be increased by the superposition of bands belonging to other elements, (Schottländer, *Ber.*, **25**, 598).

This short survey of the chemistry of the rare earths may be summarised, so far as regards the more important results, as follows:

A. Elements of the Yttrium-Cerium Groups perfectly Characterised.

Scandium.—Atomic weight 44; oxide white; salts colourless without absorption spectrum; spark spectrum rich in lines.

Yttrium.—Atomic weight 88·9 (O = 15·963) or 89·02 (O = 16); oxide white; salts colourless without absorption spectrum; spark spectrum rich in lines.

Lanthanum.—Atomic weight 138·02 (O = 15·963); oxide white; salts colourless without absorption spectrum; emission spectrum rich in lines.

Cerium.—Atomic weight 139·87 or 140·22; oxides: Ce_2O_3, CeO_2, CeO_3; salts of Ce_2O_3 colourless, without absorption spectrum; salts of CeO_2 orange-coloured.

Praseodymium.—Atomic weight 143·6; oxide greenish-white; salts green with absorption spectrum; spark spectrum rich in lines; peroxide, Pr_4O_7, dark brown.

Samarium.—Atomic weight 150; oxide white; salts yellow with absorption bands; spark spectrum rich in lines.

Gadolinium.—Atomic weight 156; oxide white; salts colourless without absorption bands; no spark spectrum (Thalén, Bettendorff); characteristic spark spectrum (Lecoq de Boisbaudran).*

Erbium.—Atomic weight 166; oxide rose-coloured; salts rose-coloured with absorption bands; spark spectrum with few and not brilliant lines (Thalén).†

Ytterbium.—Atomic weight 173; oxide white; salts colourless without absorption spectrum; spark spectrum rich in lines.

B. Elements of the Yttrium-Cerium Groups not yet thoroughly Characterised.

Didymium (neodymium).—Atomic weight 140·8; individuality doubted.

Terbium.—Atomic weight 163·1 (Lecoq de Boisbaudran, 1886); salts colourless without absorption spectrum; peroxide brownish-yellow.

Dysprosium.—Absorption spectrum, according to Lecoq de Boisbaudran, 1886, contains the following bands:—*l* 451·5, 475, 456·5, 427·5, and 804(?); Crookes gives *l* 451·5, but excludes the others (*Roy. Soc. Proc.*, **40**, 502).

Holmium.—Salts give absorption bands *l* 640·4, 536·3 (Lecoq de Boisbaudran).

Thulium.—Salts give absorption bands *l* 684, 464·5.

Zα (Lecoq de Boisbaudran, 1885) follows holmia reversion bands *l* 573, 476·12; identical with Crookes' Gδ (*C. R.*, 1886, **102**, 899).

Zβ (Lecoq de Boisbaudran, 1885) reversion bands *l* 620·5, 585·75 (double), 543·2, 487 (*C. R., loc. cit.*); apparently identical with Crookes' Gζ and probably terbia.

* The difference depends on the methods used by the experimenters.

† According to Krüss, erbia may be complex. The conclusion cannot, however, as yet be considered as proved.

Zγ (Lecoq de Boisbaudran, 1886. *C. R.*, 102, 153) follows holmia and Zα characterised by its spark spectrum.

Zε (Lecoq de Boisbaudran, 1892) follows samarium; spark spectrum lines *l* 459·3, 466·2, 462·7 (*C. R.*, **119**, 575).

Zζ (Lecoq de Boisbaudran, 1892) follows samarium reversion bands *l* 611·2 sharply defined, fading away at *l* 622 (*C. R.*, **119**, 575).

Gα (Crookes, 1886) vacuum band *l* 482.

Gβ (Crookes) vacuum band *l* 550, 541; either terbia or Lecoq's Zβ (*C. R.*, **103**, 114).

Gγ (Crookes) vacuum band *l* 568, 563.

Gδ (Crookes) vacuum band *l* 574; probably identical with Lecoq's Zα.

Gε (Crookes) vacuum band *l* 597.

Gζ (Crookes) vacuum band *l* 619; probably identical with Lecoq's Zβ.

Gη (Crookes) vacuum band *l* 647.

Sδ (Crookes) vacuum band *l* 609; gadolinium according to Bettendorff (*C. R.*, **102**, 1464; *Annalen*, **270**, 382).

Sγ (Crookes) vacuum bands *l* 456.

Unknown element with the absorption bands *l* 550 and *l* 493 in the spectrum of impure erbium; does not occur in thulium, erbium, holmium, and dysprosium (Crookes, *Roy. Soc. Proc.*, 1886, **40**, 502).

Unknown element with the absorption band *l* 475 in the didymium spectrum (Crookes, *C. R.*, **102**, 1551; Demarçay, *C. R.*, 1886, **102**, 1552).

Unknown element with the absorption band *l* 462 in the old didymium spectrum; according to Demarçay (*C. R.*, **104**, 580), it is the same element as that which gives rise to *l* 475. According to Crookes it belongs to the samarium series.

Unknown element with the absorption band *l* 434 in the old didymium spectrum (Demarçay, *C. R.*, 1886, **102**, 1552).

In 1801, Hatchett investigated a black mineral found in North America, subsequently known as columbite, and discovered in it a new element which he called columbium. In 1804, Ekeberg, when examining yttrotantalite from Ytterby and tantalite from Finland, isolated a new metallic substance which he called tantalum. Shortly afterwards Wollaston declared that columbium and tantalum were identical. Berzelius in 1815 studied tantalic acid which he at first formulated as TaO_3, but subsequently as Ta_2O_3.

In 1840, Wöhler examined the acid oxides in pyrochlore, and made known the characteristic blue colour which they give with hydrochloric

acid and zinc, and he also discovered the white volatile oxychloride. For nearly 20 years, Heinrich Rose in Berlin, and Rudolph Herman in Moscow, occupied themselves with the study of the metals of the tantalum group. I can only very briefly summarise the results of their prolonged investigations. The main conclusion of Rose's work was to show that these minerals contained the elements tantalum, giving the oxide TaO_2, and niobium, yielding the oxides NbO_2 (niobic acid, formerly known as pelopic acid) and Nb_2O_3 (hyponiobic acid, formerly called niobic acid). The chloride corresponding with NbO_2 was yellow; the hyponiobic chloride was the white substance first observed by Wöhler, and now known to be an oxychloride. Herman in 1846 believed there existed another metal, *ilmenium*, but Rose proved that the so-called ilmenic acid was a mixture of oxides of niobium. To add to the chaos, Franz von Kobell in 1860 announced the discovery of still another acid—*dianic* acid—belonging to this group. About the year 1865, however, the subject became clear through the independent researches of Marignac and Blomstrand. Marignac examined the fluoro-salts, and Blomstrand the chlorides. Both found that there existed only two metals in this group, namely, niobium and tantalum, and that the white hyponiobic chloride was an oxychloride. Blomstrand formulated niobic acid as NbO_2, and the white oxychloride $Nb_4O_3Cl_{10}$. Marignac proved the isomorphism of the hyponiobic fluoro-salts with the fluoro-salts of tin and tungsten. He found that niobium oxyfluoride was $NbOF_3$, and that in consequence hyponiobic acid became Nb_2O_5, and that the niobic acid of Rose had no existence. These conclusions were verified by the determination of the vapour density of niobic oxychloride by Troost and Hautefeuille. It was found to correspond with $NbOCl_3$ and not with Nb_2Cl_3. Rose's chloride of niobium, $NbCl_4$, was in reality $NbCl_5$. Marignac further established that the formula of tantalic acid was Ta_2O_5.

In 1858, Marignac pointed out that the fluorstannates and fluorsilicates were isomorphous. This fact settled the long discussed question of the formula of silicic acid. Prior to that time, silicic acid was usually written SiO_3, but the formula was now definitely decided to be SiO_2. The change was not only of great importance to chemistry, but produced a revolution in mineralogy. It marks, indeed, a new epoch in the history of that science.

This research was followed in 1860 by a similar examination of the fluoro-salts of zirconium, from which it became evident that the oxide of that element must be ZrO_2 instead of Zr_2O_3, as hitherto supposed. Subsequently Marignac examined the fluoro-salts of boron, tungsten, antimony, and arsenic. The research on the fluoro-salts of tungsten led to the important discovery of silicotungstic acid, which

first directed the attention of chemists to the existence of the important class of acids known as the complex mineral acids.

In examining the compounds of vanadium, Berzelius discovered a remarkable silico-vanadium-phosphoric acid. He was also the first to note the yellow precipitate which acidified ammonium molybdate gives with phosphoric acid, and which was first analysed in 1849 by Svanberg and Struve. Marignac's discovery of silico-tungstic acid again directed the attention of chemists to this class of compounds. A considerable number of such acids have now been made known by the researches of Blomstrand, Friedheim, Wolcott Gibbs, Kehrman, Péchard, Rosenheim, Scheibler, and others; but it is still very difficult to give a comprehensive theory of their constitution. It may be assumed that the complex acids contain two different negative radicles united by oxygen, and that this combining atom of oxygen is the residue of a hydroxyl group corresponding with the hydroxyl of the alcohols. To this class belongs a considerable number of salts formerly considered as double salts, but distinguished by abnormal reactions, as the chromo-oxalates, platino-oxalates, and the chromo-sulphates recently investigated by Recoura. This class of complex acids is very large, and it can hardly be doubted that salts of such acids exist in nature. Some natural borosilicates may indeed be considered as salts of complex acids; for instance, tourmaline may be represented as $B\begin{cases}(SiO_4R_3)_2\\ III\\ ORO\end{cases}$. The rare Norwegian mineral, cappelenite, may be formulated as $B\begin{cases}SiO_4Y\\ O_2Ba\end{cases}$, and the analogous and isomorphous nordenskiöldine as $B\begin{cases}SnO_4B\\ O_2Ca\end{cases}$. Boron, aluminium, and yttrium play a similar part in minerals, as may be seen on comparing the following formulæ:

$Si\begin{cases}O_2Be\\ OAlO\\ OH\end{cases}$ Euclase.

$Si\begin{cases}O_2Ca\\ OBO\\ OH\end{cases}$ Datholite.

$Fe(O-Si\begin{cases}O_2Ca\\ OBO\end{cases})_2$ Homilite.

$Fe(O-Si\begin{cases}O_2Be\\ OYO\end{cases})$ Gadolinite.

It is then probable that many of the natural aluminous silicates may be salts of alumina-silico-acids. On the basis of the researches of Tschermak, Clarke, and others, we may assume the existence of the acids $Al(SiO_4H_3)_3$ and $Al(Si_3O_8H_3)_3$. From the former, we derive an anorthite; from the latter, orthoclase. Salts of these acids are also met with in the groups of the micas and zeolites. The first acid

gives rise to such minerals as garnet, nepheline, sodalite, topaz, and andalusite. We may also conceive that ultramarine is derived from the same acid, since, according to the researches of Brögger and Bäckström, it may be formulated as $Al\begin{cases}SiO_4Na_3\\SiO_4Al\\SiO_4\end{cases}\begin{matrix}Na\\AlS\cdot S\cdot SNa\end{matrix}$

A certain number of minerals, as leucite and spodumene, are derived from $Al\begin{cases}SiO_3\\SiO_3R\end{cases}$; others, as petalite, from $Al\begin{cases}Si_3O_7\\SiO_3H\end{cases}$.

The foregoing examples will serve to show how important the study of the complex acids may become as serving to simplify the formulæ of the silicates, and in so bringing them into natural groups.

The chemistry of minerals had always great interest for Marignac, and he analysed numbers of them during the period from 1840 to 1851; many of these were collected during his travels in the Alps with his distinguished friend DesCloiseaux. His account of the analysis of æschynite is noteworthy by reason of the new analytical methods employed.

Analytical chemistry is, indeed, indebted to Marignac for a number of methods of quantitative analysis. As an example of the care with which these were worked out, I may refer to his paper on the analyses of the borates and fluorborates, in which accurate processes for the determinations of fluorine and boron, confessedly difficult quantitative operations, are given (*Zeitschr. anal. Chem.*, **1**, 405).

Geneva is especially associated with the chemistry of ozone, and Marignac had his share in proving its true nature. As far back as 1845, he showed that this substance, contrary to the statements of Williamson and Baumert, was free from hydrogen.

Few of Marignac's papers were published in English, or found their way into our journals through the medium of translations. A noteworthy exception, however, occurs in the case of a paper in the *Philosophical Magazine* for 1846, p. 527, which consists of a somewhat trenchant criticism of the well-known paper by Playfair and Joule on "Atomic Volume and Specific Gravity," read before this Society on May 17, 1845. Marignac contended that Playfair and Joule's statement "that the volume occupied by an equivalent of any salt whatever in solution in water is always an exact multiple of the number representing the atomic volume of water" has no foundation in fact, and that the experimental evidence adduced by its authors was vitiated by the arbitrary manner in which the temperatures of comparison had been selected. Marignac shows that the molecular volume of a salt in solution depends both on the temperature and on the relative pro-

portions of water and salt, and these circumstances cause the volume to vary within considerable limits. So long as these influences are neglected, or so long as we operate in such manner that they do not act in all cases in the same manner, the results obtained cannot be compared with one another. Marignac further contended that Playfair and Joule's law "that the atomic volume of any salt whatever is a multiple of 11, or of a number near to 11, or a multiple of 9·8 (the molecular volume of ice), or, again, the sum of a multiple of 11 or of 9·8," has no valid experimental foundation, and that the apparent concordance between theory and experiment is due to the arbitrary and irrational manner in which the factors 9, 8, or 11 were selected.

Marignac's criticism on Than's paper on "The Anomalous Vapour Density of Sal-ammoniac" (*Bibl. univ. Arch. sc. phys. nat.*, 1865, **22**, 5), and his own communication on "The Latent Heat of Vaporisation of Sal-ammoniac" (*C. R.*, 1868, **67**, 877), are interesting as throwing light on the nature of the change which this compound suffers on being heated—a question which has now only an historical interest, but which, 30 years ago, was of the highest importance in regard to Gerhardt's extended application of the hypothesis of Avogadro. Although no final numerical values could be obtained, the numbers which Marignac gives in the latter paper can only be explained on the assumption that the substance, on volatilisation, was almost completely resolved into its proximate constituents. It was found that the quantity of heat required to volatilise sal-ammoniac is almost exactly the same as would be required, according to the experiments of Favre and Silbermann, to decompose it. Any other conclusion would imply that sal-ammoniac possessed a heat of volatilisation absolutely anomalous when compared with that of similar substances, or that scarcely any heat was evolved by the union of its elements, that which is observed at the time of its formation being only the result of its condensation to the solid state. Similar observations by Marignac with sulphuric acid showed that the latent heat of volatilisation of this substance was practically equal to the heat of decomposition, thus substantiating the hypothesis of the decomposition of sulphuric acid by heat advanced by Wanklyn and Robinson as a result of their experiments on the diffusion of its vapour. The desire expressed by Marignac for an accurate method of measuring the heat concerned in reactions which take place at high temperatures, although not actually fulfilled, approaches realisation, and we may well hope that the methods employed by Le Chatelier, Callendar, Griffiths, and others, may find speedy application in this particular department of thermochemistry.

Marignac's most important researches in physical chemistry are,

however, concerned with his labours on the nature and process of solution. This work, involving the determination of a number of thermal magnitudes, was done with the same skill and care which he bestowed upon his stoichiometric work, and it furnishes us with a series of numerical data which are of the highest importance in regard to the general theory of the subject.

The publication of Thomsen's thermochemical researches led Marignac to communicate the results of a number of observations on the thermal effects produced by the dilution of saline solutions. He had, in fact, prior to the publication of Thomsen's work, undertaken an investigation on much the same lines, which, however, he was deterred from prosecuting, owing to the impossibility of eliminating the effects produced by the intervention of the solvent employed, and which, he maintains, had been insufficiently appreciated in researches of this character.

Marignac ascertained that for many salts the effect of dilution could be neglected, provided that solutions were used containing at most one-fortieth part of the salt; in other cases, on the contrary, the effects were perceptible not in lowering the temperature as the dilution increased, but in raising it. Such was the case with sulphuric acid, and with the acid sodium sulphate due to the decomposition of this salt by the water. When solutions of two salts which do not give rise to double decomposition are mixed, the variation in temperature is generally less than that resulting from the mixture of these solutions with water; there is usually an evolution of heat when two salts are incapable of combining with each other, absorption when they can form a double salt, variations which become, however, almost inappreciable in solutions of 1 in 40. Sulphuric acid mixed with alkali sulphates gives rise to a considerable absorption of heat. In diluting a solution containing two salts incapable of decomposing each other, the thermal effect is nearly equal to the algebraic sum of the effects which would follow on taking the salts separately. Marignac, by studying the interaction of acids and salts, proved that the action, chemical or otherwise, varies with the proportion of water in which it takes place. The thermal effect is entirely different according to the dilution; it even changes its sign in the case of sulphuric acid and sodium nitrate. Here, therefore, there is chemical decomposition between the mixed salts, and this decomposition increases with the proportion of water. The same is the case in the double decompositions of neutral salts, which appear to be the more complete the more their solutions are diluted. These phenomena would seem to receive their explanation in our modern theories of solution. We see that the interdependence between the pressure and the stability of a gaseous system, capable of dissociation, has its

analogy in a similar interdependence between the osmotic pressure and the particular phase of a changeable system in solution.

In the course of these investigations, Marignac observed the following curious anomaly. Supposing we have to dilute solutions of 1 in 10 so as to make a mixture of two substances in a solution of 1 in 80, we may either mix the two solutions of 1 in 10 directly and then add seven times the volume of water, or else first dilute each solution to 1 in 80 separately, and subsequently mix them. When the two methods were actually employed, it was found that the sum of the thermal effects was not the same. Marignac eventually discovered that the explanation was due to the alteration of the specific heats of the solutions. His method of measuring the specific heat of aqueous solutions consisted in determining the relative weights of water and of liquid under examination, that showed the same change in temperature on the addition of the same quantity of heat—a method which eliminated several external causes of error. Unfortunately, Marignac was anticipated in the prosecution of his work by Thomsen, and only the general results of his experiments were published.

The difference between the specific heat of a solution and the sum of the specific heats of its elements is the proof, and approximately the measure, of the work done by the chemical reaction causing the change of temperature of the liquid. It was established that dilution always produces contraction. When water is mixed with a solution, the coefficient of expansion of the mixture is higher than the mean of the coefficient of the two mixed liquids: it follows from this that the contraction caused by the mixture diminishes in proportion as the mixture is effected at a higher or lower temperature, and we may thence conclude that at a temperature sufficiently high the dilution of solutions will give rise neither to contraction nor to a reduction of specific heat.

In a subsequent memoir (*Bibl. univ. arch.*, 1876, **55**, 113), Marignac attempted to determine whether the specific heats of saline solutions are so connected with the nature of the acid and base that they form parallel series, such that the specific heats may be approximately calculated (as may be done in the case of densities) when the separate effect of base and acid has been determined in other salts; or whether the specific heat varies from one salt to another from causes independent of the nature of acid and base. If the latter alternative be established, it becomes necessary to ascertain the relation between the variations in specific heat and some other property of the salts, in particular their tendency to form definite crystalline hydrates. After two years' continuous labour during which he frequently made as many as a dozen observations a day, he found that the specific

heat of saline solutions always increases with the temperature, and in proportion to the degree of concentration of the solutions. This increase is very rapid in the case of certain solutions, *e.g.*, copper sulphate, but the specific heat does not exclusively depend on the nature of the acid and base, and has apparently no relation to the greater or less tendency of salts to combine with water to form definite crystallisable hydrates. It seems rather to be related to the existence of definite but dissociated hydrates, the proportion of which varies with that of the water and with the temperature.

In this connection we may refer to Marignac's work on the solubility of calcium sulphate in water. Having accidentally observed that a solution of this salt contained more of the substance than corresponded with its supposed solubility, he was led to find that its solubility increases from 0° to 32°, attains a maximum between 32° and 41°, and then diminishes. The phenomena of supersaturation of calcium sulphate were identical in kind with those observed in the case of sodium sulphate.

When we have regard to the amount of work which has been bestowed upon it, no field of research in chemical physics has proved less fruitful than that of liquid diffusion. In spite of much laborious investigation, the subject remains very much as Graham left it, and although a great amount of experimental matter has been accumulated, few broad general principles, other than those which our first President made known, have been obtained. Marignac brought all the qualities of patient industry, manipulative skill, and a rigorous sense of accuracy to the elucidation of the problem, especially in regard to the simultaneous diffusion of mixed substances. He attempted to estimate the relative coefficient of diffusion of two salts from measurements of their simultaneous diffusion. But the main outcome of a prolonged investigation was to establish that the mixture of two substances always diminishes the diffusibility of the less diffusible of the two. He found that it was immaterial whether mixtures of equal weights or mixtures of equivalent proportions were operated upon. The degree of concentration of the solution had a variable influence on the relative coefficient of simultaneous diffusion, sometimes increasing with increasing dilution, sometimes remaining unchanged, and sometimes diminishing as the proportion of water to salt is increased. The most important general result is that the rates of diffusion of the acids are related to those of the metals in such manner that the salts of any specified acid always follow in the same order whatever the acid may be, and that all the salts of any metal follow in the same order, independently of the nature of the metal. The following table shows the order of the diffusion coefficients.

Cl, Br, I	H
NO_3	K,NH_4
ClO_3, ClO_4, MnO_4	Ag
F	Na
CrO_4	Ca, Sr, Ba, Pb, Hg.
SO_4	Mn, Mg, Zn
CO_3	Cu
	Al

The analogy which this table manifests to that of the conductivity of salt solutions is highly suggestive in relation to our present conceptions of the true nature of solution (compare Ostwald, *Solutions*, p. 139).

It is significant of his grasp of principles, and of the logical order of his thought, that Marignac, during the memorable discussion that took place before the Académie des Sciences, at Paris, in May and June, 1877, on equivalency and atomic weights, should have taken up a position which is in entire accord with that which we occupy at present. His contention, which at that time brought him into direct conflict with Berthelot, more particularly in regard to the criteria which should guide chemists in the selection of the several possible atomic weights that chemical considerations alone would serve to indicate, expresses the settled conviction of to-day.

Modest, patient, and unassuming, transparent in character, and honest of purpose, with no other conception of his calling than that of pursuing truth for truth's sake, Marignac lived wholly for science, and no man has served her with a purer or more unselfish devotion. If the world of science is the poorer by his loss, it is the richer by his example.

Titles of Marignac's Published Papers.

Analyse du minerai de cobalt de la mine appelée "la Sophie" (Grand-Duché de Bade), *Annales des mines*, **18**, 1840, pp. 153—160.

Produits de l'action de l'acide nitrique sur la naphtaline, *Bibl. univ.*, **32**, 1841, pp. 317—328; *Annalen*, **38**, 141, pp. 1—13.

Sur un produit liquide qui se forme dans la préparation de l'acide naphtalique, *Bibl. univ.*, **32**, 1841, pp. 328—334; *Annalen*, **38**, 1841, pp. 13—20.

Note sur l'acide naphtalique, *Bibl. univ.*, **36**, pp. 370—384; *Annalen*, **42**, 1842, pp. 215—226.

Description d'une machine soufflante à colonne d'eau, *Annales des mines*, **1**, 1842, pp. 69—84.

Sur les poids atomiques du chlore, du potassium et de l'argent, *Bibl. univ.*, **40**, 1842, pp. 145—158; *Erdm. J. pr. Chem.*, **26**, 1842, pp. 304—307; *Annalen*, **44**, 1842, pp. 11—25; Paris, *Compt. rend.*, **14**, 1842, pp. 570—573.

Sur la décomposition par la chaleur du chlorate, du perchlorate, du bromate et de l'iodate de potasse, *Bibl. univ.*, **45**, 1843, pp. 347—357.

Analyses diverses destinées à la vérification de quelques équivalents chimiques, *Bibl. univ.*, **46**, 1843, pp. 350—377.

Quelques conséquences de la loi de Prout, *Schweizer. Gesell. Verh.*, 1843, pp. 62—66.

Analyses de quelques substances minérales (Pennine, chlorite hexagonale), par Marignac et Alfred Descloiseaux, *Ann. Chim. Phys.*, **10**, 1844, pp. 427—433; *Bibl. univ.*, **49**, 1844, pp. 131—141.

Analyses de la Greenovite, *Bibl. univ.*, **53**, 1844, pp. 390—391.

Notices minéralogiques (Gismondine et Phillipsite, Greenovite, Disthène et Staurotide du St. Gothard, Chrichtonite, Fer titané de Washington, Chlorite, Chlorite de Traverselle), *Ann. Chim. Phys.*, **14**, 1845, pp. 41—61.

Sur la production et la nature de l'ozone. Paris, *Compt. rend.*, **20**, 1845, pp. 808—810; *Ann. Chim. Phys.*, **14**, 1845, pp. 252—255; *Bibl. univ., Archives de l'électricité*, **5**, 1845, pp. 5—11; *Journ. de Pharm.*, **7**, 1845, pp. 450—454; *Walker, Electr. Mag.*, **2**, 1846, pp. 56—57.

Sur les relations qui existent entre les propriétés physiques et la composition chimique des corps composés, *Bibl. univ., Archives*, **1**, 1846, pp. 1—29, 137—162.

Remarques sur le mémoire de Ch. Gerhardt relatif au poids atomique du chlore, *Bibl. univ., Archives*, **1**, 1846, pp. 53—60; *Annalen*, **59**, 1846, pp. 284—290.

On Messrs. Lyon Playfair and Joule's Memoir on Atomic Volume and Specific Gravity (Transl.), *Phil. Mag.*, **28**, 1846, pp. 527—532.

Notices minéralogiques (Epidote, Humite ou Chondrolite du Vésuve, Pinite, Gigantolite), *Bibl. univ., Archives*, **4**, 1847, pp. 148—162; *Journ. de Pharm.*, **12**, 1847, pp. 150—152.

Notices minéralogiques (Liébénérite, Diaspore cristallisé du St. Gothard; Tourmaline, forme nouvelle; Mica, Pleónaste métamorphosé de Monzoni), *Bibl. univ., Archives*, **6**, 1847, pp. 293—304; *Journ. de Pharm.*, **13**, 1848, pp. 290—292.

Sur les poids atomiques du cérium, du lanthane et du didyme, *Bibl. univ., Archives*, **8**, 1848, p .265, *et* **11**, 1849, pp. 21—30; *Ann. Chim. Phys.*, **27**, 1849, pp. 209—231; *Erdm. J. pr. Chem.*, **48**, 1849, pp. 406—424; *Annalen*, **71**, 1849, pp. 306—314.

Sur la composition et les formes cristallines des nitrates de protoxyde de mercure. Genève, *Mém. Soc. phys.*, **12**, 1849, pp. 233—254; *Ann. Chim. Phys.*, **27**, 1849, pp. 315—333; *Annalen*, **72**, 1849, pp. 55—73; *Bibl. univ., Archives*, **12**, 1849, p. 51.

Recherches sur l'azoture de bore. Genève, *Mém. Soc. phys.*, **12**, 1849, pp. 357—380; *Bibl. univ., Archives*, **17**, 1851, pp. 159—160; *Annalen*, **79**, 1851, pp. 247—248.

Remarques à l'occasion d'un mémoire de M. Delafosse: "Sur une relation importante qui se manifeste, en certains cas, entre la composition atomique et la forme cristalline des minéraux," *Bibl. univ., Archives*, **17**, 1851, pp. 33—46.

Note sur les expériences de M. Foucault, relatives à la déviation du plan d'oscillation du pendule produite par la rotation de la terre, *Bibl. univ., Archives*, **17**, 1851, pp. 116—130.

Analyse d'un calcaire hydraulique exploité près de Thonon (Chablais) ou du ciment-pierre de la Drance, *Bibl. univ., Archives*, **18**, 1851, pp. 50—53.

Recherches sur le didyme et sur ses principales combinaisons, *Ann. Chim. Phys.*, **38**, 1853, pp. 148—177; *Erdm. J. pr. Chem.*, **59**, 1853, pp. 380—404; *Bibl. univ., Archives*, **24**, 1853, p. 278.

Recherches sur la congélation et l'ébullition des hydrates de l'acide sulfurique, *Bibl. univ., Archives*, **22**, 1853, pp. 225—239; *Ann. Chim. Phys.*, **39**, 1853, pp. 184—196; *Erdm. J. pr. Chem.*, **61**, 1854, pp. 45—55.

Ueber Schwefelsaures Nickeloxydul, *Annalen*, **97**, 1856, pp. 294—295.

Recherches sur les formes cristallines de quelques composés chimiques. Paris, *Compt. rend.*, **42**, 1856, pp. 288—290; Genève, *Mem. Soc. Phys.*, **14**, 1858, pp. 202—286; *Bibl. univ., Archives*, **31**, 1856, pp. 170—172.

Recherches sur les formes cristallines et la composition chimique de divers sels, *Annales des mines*, **9**, 1856, pp. 1—51; **12**, 1857, pp. 1—74; **15**, 1859, pp. 221—290; *Bibl. univ., Archives*, **36**, 1857, pp. 207—209.

Sur les relations existant entre certains groupes de formes cristallines appartenant à des systèmes différents. Paris, *Compt. rend.*, **45**, 1857, pp. 650—652.

Sur les équivalents chimiques du baryum, du strontium et du plomb, *Bibl. univ., Archives*, **1**, 1858, pp. 209—227; *Erdm. J. pr. Chem.*, **74**, 1858, pp. 209—218; *Annalen*, **106**, 1858, pp. 165—171.

Sur l'isomorphisme des fluosilicates et des fluostannates et sur le poids atomiques du silicium. Paris, *Compt. rend.*, **46**, 1858, pp. 854—857; *Bibl. univ., Archives*, **2**, 1858, pp. 89—101; *Erdm. J. pr. Chem.*, **74**, 1858, pp. 161—164; *Annalen*. **107**, 1858, pp. 94—96.

De l'application de l'étude des formes cristallines à la recherche des poids atomiques des corps simples et des formules atomiques des corps composés, *Bibl. univ., Archives*, **6**, 1859, pp. 105—124.

Sur le poids atomique du graphite trouvé par Brodie, *Bibl. univ., Archives sc. phys. nat.*, **8**, 1860, pp. 30—40.

Recherches sur les fluozirconates et sur la formule de la zircone. Paris, *Compt. rend.*, **50**, 1860, pp. 952—955; *Bibl. univ., Archives sc. phys. nat.*, 1860, pp. 121—125; *Erdm. J. pr. Chem.*, **80**, 1860, pp. 426—429; *Annalen*, **116**, 1860, pp. 359—364.

A propos des recherches de Stas sur les rapports réciproques des poids atomiques, *Bibl. univ., Archives sc. phys. nat.*, **9**, 1860, p. 97—107.

Recherches chimiques et cristallographiques sur les fluozirconates. Formule de la zircone, *Ann. Chim. Phys.*, **60**, 1860, pp. 257—307; *Erdm. J. pr. Chem.*, **83**, 1861, pp. 201—309.

Ueber die Analyse der borsauren Salze und der Fluorbor-Verbindungen, *Zeitschr. anal. Chemie*, **1**, 1862, pp. 405—410; *Chem. News*, **8**, 1863, pp. 75—76.

Recherches sur les tungstates, les fluotungstates et les silicotungstates. Paris, *Compt. rend.*, **55**, 1862, pp. 888—892; *Annalen*, **125**, 1863, pp. 362—367.

Recherches chimiques et cristallographiques sur les tungstates, les fluotungstates et les silicotungstates, *Ann. Chim. Phys.*, **69**, 1863, pp. 5—86.

Forme cristalline du sulfate de thorine, *Bibl. univ., Archives sc. phys. nat.*, 18, 1863, p. 345.

Recherches sur les acides silicotungstiques et note sur la constitution de l'acide tungstique, *Ann. Chim. Phys.*, **3**, 1864, pp. 5—76; *Bibl. univ., Archives sc. phys. nat.*, **20**, 1864, pp. 5—14; *J. pr. Chem.*, **94**, 1865, pp. 356—380; Paris, Acad. Sc., *Compt. rend.*, **58**, 1864, pp. 809—812; *Annalen*, **132**, 1864, pp. 25—31.

Considérations théoriques à l'occasion du mémoire de M. Karl Than: "Sur la densité anomale de la vapeur du sel ammoniac," *Bibl. univ., Archives sc. phys. nat.*, **22**, 1865, pp. 5—14.

Description des formes cristallines des molybdates alcalins, *Bibl. univ., Archives sc. phys. nat.*, **23**, 1865, pp. 5—25.

Recherches sur les combinaisons du niobium, *Bibl. univ., Archives sc. phys. nat.*, **23**, 1865, pp. 167—182, 249—282; *Annalen*, Suppl. Bd., **4**, 1865—1866, pp. 273—350; *J. pr. Chem.*, **97**, 1866, pp. 449—465.

Remarques sur le mémoire de M. Stas, intitulé: "Nouvelles recherches sur les lois des proportions chimiques, etc.," *Bibl. univ., Archives sc. phys. nat.*, **24**, 1865, pp. 371—376; *Annalen*, Suppl. Bd., **4**, 1865—1866, pp. 201—206; *Ann. Chim. Phys.*, **9**, 1866, pp. 243—248; *Chem. News*, **14**, 1866, pp. 279—280.

Sur les combinaisons hyponiobiques. Paris, Acad. Sc., *Compt. rend.*, **60**, 1865, pp. 234—237; *Annalen*, **135**, 1865, pp. 49—54; *J. pr. Chem.*, **94**, 1865, pp. 304—308.

Sur la constitution de l'acide hyponiobique et de l'acide tantalique et sur leur association dans le règne minéral. Paris, Acad. Sc., *Compt. rend.*, **60**, 1865, pp. 1355—1357; *Annalen*, **136**, 1865, pp. 295—298.

Recherches sur les combinaisons du niobium, *Bibl. univ., Archives sc. phys. nat.*, **25**, 1866, pp. 5—33; *Ann. Chim. Phys.*, **8**, 1866, pp. 5—75.

Recherches sur les combinaisons du tantale, *Bibl. univ., Archives sc. phys. nat.*, **25**, 1866, pp. 5—33; *Ann. Chim. Phys.*, **8**, 1866, pp. 5—75.

Recherches sur les combinaisons du tantale, *Bibl. univ., Archives, sc. phys. nat*, **26**, 1866, pp. 89—116; Paris, Acad. Sc., *Compt. rend.*, **63**, 1886, pp. 85—87; *Annalen*, Suppl. Bd., **4**, 1865—1866, pp. 350—377; **140**, 1866, pp. 153—156; *Ann. Chim. Phys.*, **9**, 1866, pp. 249—276.

Sur quelques fluosels de l'antimoine et de l'arsenic, *Bibl. univ., Archives sc. phys. et nat.*, **28**, 1867, pp. 5—19; *Ann. Chim. Phys.*, **10**, 1867, pp. 371—385; *Annalen*, **145**, 1868, pp. 237—253.

Essais sur la séparation de l'acide niobique et de l'acide titanique. Analyse de l'œschynite, *Bibl. univ., Archives sc. phys. nat.*, **29**, 1867, pp. 265—291; *J. pr. Chem.*, **102**, 1867, pp. 448—454; *Ann. Chim. Phys.*, **13**, 1868, pp. 5—29.

Ueber Hermann's Untersuchungen, das Niobium, Tantal, und Ilmenium betreffend, *J. pr. Chem.*, **101**, 1867, pp. 459—468.

Recherches sur la réduction du niobium et du tantale, *Bibl. univ., Archives sc. phys. nat.*, **31**, 1868, pp. 89—103; Paris, Acad. Sc., *Compt. rend.*, **66**, 1868, pp. 180—183; *J. pr. Chem.*, **106**, 1869, pp. 152—155.

Sur la chaleur latente de volatilisation du sel ammoniac et de quelques autres substances, *Bibl. univ., Archives sc. phys. nat.*, **33**, 1868, pp. 169—198; Paris, Acad. Sc., *Compt. rend.*, **67**, 1868, pp. 877—880; *Deut. Chem. Ges. Ber.*, 1868, pp. 262—263; Paris, *Bull. Soc. Chim.*, **11**, 1869, pp. 225—227; *Annalen*, **149**, 1869, pp. 351—356; *Phil. Mag.*, **37**, 1869, pp. 318—320.

De l'influence de l'eau sur les doubles décompositions salines et sur les effets thermiques qui les accompagnent, *Bibl. univ., Archives sc. phys. nat.*, **36**, 1869, pp. 319—337; Paris, Acad. Sc., *Compt. rend.*, **69**, 1869, pp. 1180—1183; *Annalen*, **155**, 1870, pp. 185—204; *Zeit. f. Chem.*, **6**, 1870, pp. 69—71.

Recherches sur les chaleurs spécifiques, les densités et les dilatations de quelques dissolutions, *Bibl. univ., Archives sc. phys. nat.*, **39**, 1870, pp. 217—249, 273—303; *Ann. Chim. Phys.*, **22**, 1871, pp. 385—444; *Phil. Mag.*, **41**, 1871, pp. 134—153.

De l'influence prétendue de la calcination sur la chaleur de dissolution des oxydes métalliques, *Bibl. univ., Archives sc. phys. nat.*, **42**, 1871, pp. 209—219.

Notices chimiques et cristallographiques sur quelques sels de glucine et des métaux de la cérite, *Bibl. univ., Archives sc. phys. nat.*, **46**, 1873, pp. 193—217; *Ann. Chim. Phys.*, **30**, 1873, pp. 45—69.

Sur la solubilité du sulfate de chaux et sur l'état de sur saturation de ses dissolutions, *Bibl. univ., Archives sc. phys. nat.*, **48**, 1873, pp. 120—128.

Sur la diffusion simultanée de quelques sels, *Bibl. univ., Archives sc. phys. nat.*, **50**, 1874, pp. 89—122; *Ann. Chim. Phys.*, **2**, 1874, pp. 546—581.

Sur les chaleurs spécifiques des solutions salines, *Bibl. univ., Archives sc. phys. nat.*, **55**, 1876, pp. 113—135; *Ann. Chim. Phys.*, **8**, 1876, p. 410.

Sur les équivalents chimiques et les poids atomiques comme base d'un système de notation, *Bibl. univ., Archives sc. phys. nat.*, **59**, 1877, pp. 233—249; *Moniteur scientifique*, **7**, p. 920.

Observations à propos d'une lettre de M. Berthelot à M. de Marignac sur les systèmes de notations chimiques, *Bibl. univ., Archives sc. phys. nat.*, **60**, 1877, pp. 343—350.

Sur les terres de la gadolinite, *Bibl. univ., Archives sc. phys. nat.*, **61**, 1878, pp. 283—295; *Ann. Chim. Phys.*, **14**, 1878, pp. 247—258; *Chem. News*, **38**, p. 215.

L'ytterbine, terre nouvelle contenue dans la gadolinite, *Bibl. univ., Archives sc. phys. nat.*, **64**, 1878, pp. 87—107. Paris, *Compt. rend.*, **87**, p. 578.

Sur les terres de la samarskite, *Bibl. univ., Archives sc. phys. nat.*, **3**, 1880, pp. 413—438; Paris, *Compt. rend.*, **90**, 1880, pp. 899—903; *Ann. Chim. Phys.*, **20**, 1880, p. 535.

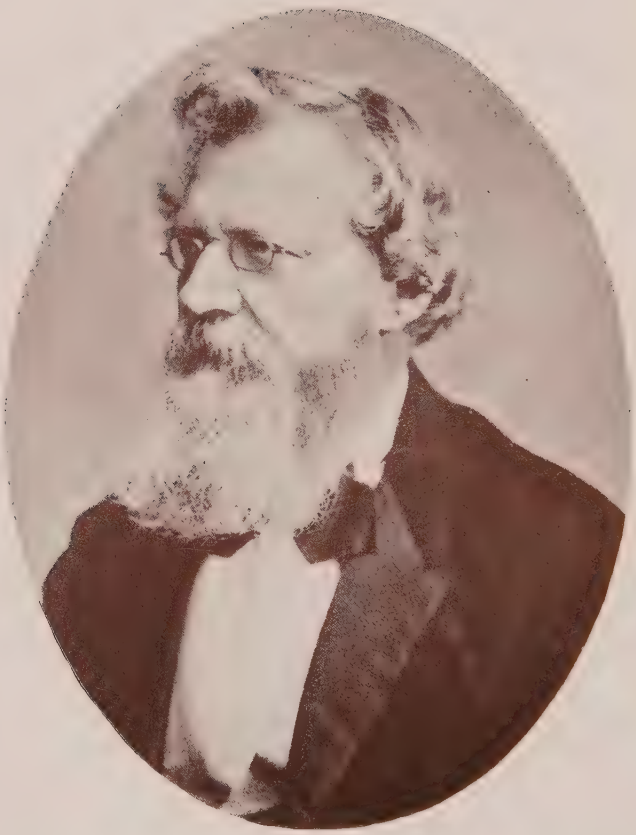
Vérification de quelques poids atomiques: bismuth, manganèse, magnésium et zinc, *Bibl. univ., Archives sc. phys. nat.*, **10**, 1883, pp. 5—27 et 193—224; *Rec. des Travaux Chimiques des Pays-Bas*, **3**, p. 310.

Sur une prétendue association par cristallisation de corps n'offrant aucune analogie de constitution atomique, *Bibl. univ., Archives sc. phys. nat.*, **11**, 1884, pp. 399—407; *Bull. Soc. Chim.*, **41**, 1884, p. 541; *Deut. Chem. Ges. Ber.*, 1884, p. 2831.

Proportion de matière organique contenue dans l'eau du Rhône, *Mémoires de la Soc. de physique et d'hist. nat. de Genève*, t. **29**; 1re partie, *Bibl. univ., Archives sc. phys. nat.*, **11**, 1884, pp. 538—540.

Réflexions sur le groupe des terres rares, *Bibl. univ., Archives sc. phys. nat.*, **17** 1887, pp. 373—389.

Charles Marignac



A. W. v. Hofmann

A. W. Hofmann

HOFMANN MEMORIAL LECTURE.*

(Delivered May 5th, 1893.)

Personal Reminiscences of Hofmann and of the conditions which led to the establishment of the Royal College of Chemistry and his appointment as its Professor.

By Lord Playfair, G.C.B., F.R.S., &c.

I believe it is desired that I should show what were the conditions that led up to a separate College of Chemistry in this country under the illustrious Hofmann, and that I should preface my remarks by some memories of the great chemist's early days at the famous University in Giessen, where I studied with him. My few words will only be introductory to the more valuable observations of those chemists who worked and co-operated with him in this country.

Hofmann was about two years my senior in age; nevertheless he did not begin his chemical training in Liebig's laboratory till after I had left it. Chemistry was not the profession which it was originally desired that he should follow. He first intended to pursue a career in philology and law, and studied these subjects at the University, and his training in languages stood him in good stead in after life; indeed, I have heard him make excellent speeches in several languages—I recollect one instance especially, in 1867, when the French chemists gave a memorable banquet to the chemists of foreign countries: I was entrusted with the thanks of the invited guests, and spoke in English, while Hofmann, in proposing the health of the French chemists, made a capital French speech.

When I first knew Hofmann at Giessen he was studying mathematics and physics, and, though he mixed in a friendly way with the active investigators in Liebig's laboratory, he was not one of our body. When he did enter that great laboratory, he had a groundwork of general culture and physical science that helped him greatly in his subsequent career. With that I have nothing to say except in relation to his influence on English chemistry.

But I must diverge from the immediate subject of my memoir to recall to mind the position of English chemistry, in order to explain why the advent of Hofmann to this country became such an important

* Chemical Society's Memorial Lectures, No. III. Compare *Proceedings of the Chemical Society*, 1893, p. 132.

event. England has never been deficient in great chemical investigators, but has lacked practical schools for training them. Indeed we can claim with perfect justice that a large number of the discoveries which have made chemistry a science have originated in this country. The last century was especially prolific. The capital discovery of oxygen and the other pneumatic discoveries of Priestley; the studies of airs and of latent heat by Black; the discovery of the composition of water simultaneously by Cavendish and Wedgwood; the work of Dalton, extending into the last and present century, by which he brought law and order into our ideas of chemical combination: all these were radical discoveries forming the very foundations of chemistry.

In the present century I have again to begin with Dalton, for it was my good fortune to know him intimately, and I can never forget his venerable figure, supported on the arm of Dr. Joule, coming daily to hear my lectures at Manchester on the new organic chemistry, which had arisen in then recent times. Dalton, Davy, Faraday, and Graham indeed stand out as shining lights in our century. Davy and Faraday were brilliant investigators, and both of them had a singular charm and eloquence as lecturers. To them we owe largely the popularity of chemistry in this country. But none of these chemists, except Graham, thought of opening their laboratories for the training of students in the methods of research. That was reserved to my own master, the celebrated Thomas Graham. I was a student in his laboratory in Glasgow in 1835 and 1836, and followed him to London as his private laboratory assistant in University College. Graham's example spread, and several Colleges, and even the Universities, slowly adopted the view that laboratories were necessary to teach and to train the chemists of the future.

At that time organic chemistry was little known or studied in this country, and all of us who had means to go abroad used to flock either to the laboratory of Liebig at Giessen or to that of Wöhler at Göttingen. I need not point out that Baron Liebig exerted an enormous influence on the progress of organic chemistry, both by his own discoveries and by those of his pupils from all countries, who were trained to do researches in his celebrated laboratory. Many English students studied in it, and when they returned to England they were imbued with the enthusiasm of their master, and acted as missionaries in spreading a knowledge of the new organic chemistry. Soon laboratories for teaching students were opened in various parts of the country.

In 1840 Liebig published his celebrated work, *Chemistry of Agriculture and Physiology*. It is difficult to-day to realise the effect that work had in promoting the study of chemistry: it greatly

increased, the demand for laboratory teaching and even the older universities found it necessary to provide means for laboratory training.

Two years after its publication, in 1842, the illustrious Baron Liebig made a sort of triumphal tour in this country. He visited the Prime Minister, Sir Robert Peel, at Drayton Manor, and paid other visits to the great agriculturists of the day—Lord Spencer, Lord Ducie, Lord Fitzwilliam, Mr. Pusey, and many others, as well as to most of the chief towns. At all places meetings were held, and Liebig, with his travelling companion, the genial and celebrated geologist, Dr. Buckland, had opportunities of disseminating his views on the importance of chemistry to mankind. The tour was a personally conducted one, like Cook's tours in the present day: the conductor and interpreter of the party, in fact, was a young man called Lyon Playfair, who took care that the effects of the tour should be felt in all the chief centres of Great Britain.

The immediate effect of Liebig's tour was to make chemistry a popular science, and to induce colleges to open laboratories for teaching it. The School of Mines was opened in Jermyn Street with, for the time, an excellent laboratory, which was always filled with students; still, its purposes were chiefly limited to the professional objects of the college. University College and King's College gave much attention to laboratory teaching. The popular wave of 1842–43 did not soon expend its force, and in 1845 the Royal College of Chemistry arose.

I have mentioned these facts to show that the time had come to open a special college of chemistry. It could not have been created sooner than it was, because the demand would have been too limited. Two wise men deserve the chief credit for its foundation: I need scarcely say that they were the Prince Consort and the Queen's physician, Sir James Clark. As I had the honour and privilege of a long continued friendship with both of these great men, I may with advantage explain their reasons for desiring to found a special college of chemistry. They saw that all the chemical laboratories in existence in this country were mere accessories or subordinates to professional training; the students who entered them rarely desired to become chemists, but only wished to learn as much of the science as would be useful to them in their professions of doctors, lawyers, or engineers. This limitation sometimes took an exaggerated form, as it did in the case of a Turk, for example, who joined my laboratory and then told me he wished to learn no more chemistry than would help him to explain the doctrines of Paracelsus. The promoters of the Royal College of Chemistry therefore desired to found an institute apart from professional requirements, in which chemistry would be

studied for its own sake, with the expectation that many students might follow it as the occupation of their lives, and have an ambition to widen its boundaries by research. A college of this kind, without endowments, could not have been created unless there had been a strong popular feeling in its favour, and I have tried to show how that arose through Liebig's influence.

Science belongs to no country, and the reputation of Hofmann and the recommendation of Liebig clearly pointed him out as the director of the new college. He had qualifications of a remarkable kind for the position. As a teacher he was singularly interesting and lucid. He marshalled his arguments with great care, and as he brought them towards the conclusion, he increased in his persuasiveness and seemed to each individual student to take him into his special confidence as to the result. The lucidity of his explanations was admirable. I would quote as an instance his lecture on the metrical system of weights and measures; this lecture was the very best exposition of the subject that I have heard. A lucid power of exposition was essential to the teacher of a special school of science, but it was not the chief element of Hofmann's success. Enthusiastic as an investigator of scientific problems, he could impart his enthusiasm, if not his genius, to others: his pupils were led to extend his researches with great success, and to enlarge the boundaries of science in the directions which he indicated. If the College of Chemistry were as successful as I claim it to be, you may ask why did it disappear? It had no endowments, and depended to some extent on popular subscriptions. These were easy to obtain when chemistry had the temporary popularity which I described. Every landowner then thought that agricultural chemistry was to be his salvation. Liebig's book was not a muck manual, and did not produce the expected results; the College of Chemistry, however, went on its even course of promoting science for its own sake, but the support gradually dwindled.

At this time, fortunately, I resigned my professorship, and Hofmann succeeded me, carrying with him his college as the laboratory of the School of Mines. This was inevitable under the circumstances, but it was not good for the College of Chemistry or for science. The original success of the college was due to its separate and independent existence: its absorption into the School of Mines contracted its original ideas, and made it subordinate to professional needs. No doubt Hofmann felt this, for he left England in 1864 to take up a professorship in Berlin.

I hope that I am not too sanguine, but I should like to live to see a new college or institute of chemistry arise, like a Phœnix, from the ashes of the old one. Will the new Commission for a London

University stir among the not yet cold ashes of the old College, and allow the Phœnix to escape? If it is to be permanent, it must rest on endowment, and science will find another great man to act as Director. Such aspirations may not improbably be carried into effect, though their realisation may be delayed. When Lawes, with true munificence, determined to benefit agriculture by laboratory research, a Gilbert was at hand capable of carrying out his ideas. We may hope that the Chemical College of Hofmann may appear again in a new and more permanent form in connection with higher university teaching in London, as a supplement to, and not in competition with, the excellent laboratories in our colleges.

I now yield my place to the pupils of Hofmann. They will tell you how precious his labours have been to the advancement of the science which we love. This is of infinitely more importance to the world than the incidental advantages which flow from the practical applications of abstract science. Nevertheless Dr. Perkin will, no doubt, tell you some interesting and startling facts in relation to these. Hofmann's first research in the Giessen laboratory was upon the nature of coal tar. When he became Director of the College of Chemistry, he continued his researches, thinking of science only, not of practice. From them arose the great tar industry, especially in its relations to the production of colours. Though these originated in this country as an important industry, the Germans, from their better technical education, have now secured nearly nine-tenths of the production of artificial colours.

Hofmann's discoveries are our heritage in science. It is useful to us all to hold such an In Memoriam celebration as this. In reviewing Hofmann's successful life, which has so enriched the fields in which he laboured, both old and young feel that we should like to live as he lived. In thinking of Hofmann, I recall one of my favourite verses, by Bailey.

> "We live in deeds not years; in thoughts not breaths,
> In feelings, not in figures on a dial.
> We should count time by heart throbs. He most lives
> Who thinks most, feels the noblest, acts the best."

E.

The History of the Royal College of Chemistry and Reminiscences of Hofmann's Professorship.

By Sir F. A. Abel, Bart., K.C.B., F.R.S., &c.

Not from any unwillingness to undertake what can only be regarded as a labour of love, but from a conviction of the inadequacy of my powers, under overwhelming pressure of official work, to worthily accomplish that labour, have I hesitated to accept the task which my colleagues of the Chemical Society, and old fellow students of the Royal College of Chemistry, have pressed upon me, of placing on record some incidents connected with the earlier part of the career in London, of my beloved and revered master and friend, the late August Wilhelm von Hofmann. And, when I recall to mind the interesting account of the difficulties overcome in securing to England the services of the courageous and enthusiastic worker—that masterly organiser and matchless teacher—which his distinguished pupil, Dr. Tiemann, included in the admirable memorial-address delivered to the German Chemical Society last autumn, and the graphic outline which Hofmann, the real founder of the College of Chemistry, himself published, in 1871, of the early history of that school, under the title of *A Page of Scientific History*, I feel that it will indeed be difficult to impart to my brief recital any semblance of novelty, or any interest, additional to that which, for his many pupils, admirers and friends, invests all the circumstances of Hofmann's career, or which may, perhaps, attach to such circumstances as that the narrator of this fragmentary sketch was one of the first students whose names were inscribed upon the register of the College of Chemistry, even before the services of Hofmann had been secured to it; that he was the first fortunate individual who was selected by the master from his pupils as assistant, and that, during the first five years of the struggling but vigorous existence of the New National School of Chemistry, it was his privilege and pride humbly to imitate, to the utmost of his youthful powers, the indefatigable devotion of the enthusiastic teacher to the interests of the School and its students, and, at the same time, to carry on the experimental work connected with some of the brilliant researches which, during that period shared, with his pupils, the untiring energies of that prince of investigators and giant for work.

To Lord Playfair, the fellow student, colleague, and firm friend of Hofmann, we are greatly indebted for the interesting sketch with which he has favoured us, of the position of chemical instruction in

Great Britain at the period when the idea was first conceived, fifty years ago, of establishing an English School of Practical Chemistry, upon the basis of Liebig's School at Giessen, which, at that time, had acquired a world-wide reputation, and to which students resorted from all parts of the world.

The commencement of my own career as a chemist affords no bad illustration of the difficulties attending attempts by young beginners with very limited resources, to acquire a knowledge of practical and analytical chemistry, with a view to adopting the science as a profession, half a century ago. The two or three establishments where chemical tuition was pursued to a very limited extent, were closed to young aspirants of that class; and, when my father remained undeterred by the advice which my subsequent good friend, the late Robert Warington, gave him, not to think of letting his son pursue the study of chemical science as a future means of livelihood, on account of the very limited prospects of advancement in the profession, the Royal Polytechnic Institution presented itself to him as the only place at which the fees demanded were within his means. I accordingly entered the laboratory of that dispensary of so-called popularised science, dazzled by the prospects of a brilliant future, presented to me by the clever popular lecturer of that time: only, to find that not even an attempt was made to impart to the deluded youngster the fragmentary superficial information of the Professor, and that the sole means which were left to him of acquiring some practical chemical knowledge, consisted in plodding, unaided, through Brande's *Manual*, endeavouring to acquire experimental skill by preparing the elements and their compounds, according to the directions there laid down, and to become acquainted with analysis by following the instructions for applying tests given in tabular form by Andrew Parnell. At the expiration of six months' struggle to work steadily in this fashion, amid surroundings by no means conducive to perseverance, I quitted the Institution (in February, 1845), armed with a testimonial certifying that my "analyses and experiments had always been conducted with great skill and minuteness," and that the Professor could "confidently recommend Mr. Abel to any appointment where a knowledge of practical chemistry may be required." Failing to realise that my practical chemical education had attained the degree of completeness pourtrayed by this description, I hailed with joy the tidings that a School of Chemistry was about to be established in London upon the Giessen type. Several other young men, who afterwards became prominent pupils of Hofmann, were in a similar position at that time, and so, when the temporary laboratories of the new college were opened in the autumn of 1845, there was a small band of aspirants impatiently waiting to

avail themselves of the benefits of the system of instruction which had already acquired so high a reputation on the Continent.

The importance of establishing in England an institution where the systematic study of chemistry, as a profession in itself, could be pursued, and where not only the acquirement of proficiency in systematic chemical analysis, but also the attainment of a knowledge of the art of chemical research, could be placed within the reach of a student of moderate means, had then become recognised by some prominent public-spirited men in England, mainly, in the first instance, through the intelligent representations and indefatigable exertions of Dr. John Gardner, the translator of the admirable little work of Liebig's, entitled *Familiar Letters on Chemistry*, which most usefully contributed to awaken the public mind to the benefits to be derived from the pursuit of chemical research. Dr. Gardner was zealously assisted in his first endeavours to place the scheme upon a practical footing, by his intimate friend, Mr. J. Lloyd Bullock, one of Liebig's earlier pupils, a fellow student of Hofmann's at Giessen, who, already in 1843, was the head of a prominent pharmaceutical business in Conduit Street, and is now, at the ripe age of 82, almost as hale and active in mind and body as he was in those days. He recently directed my attention to the following incident in the early history of the College of Chemistry, of which I believe very few of those who have since been connected with that school have any knowledge.

The sympathies of a number of prominent men had been enlisted, and promises of substantial support obtained, in 1843, in favour of a proposal to establish in London a National Practical School of Chemistry, by means of a very skilfully prepared prospectus; it was there pointed out that the progress of Liebig's Giessen School had been watched with deep interest in England, where the researches of that great chemist and his pupils had already given a most important impetus to agriculture and national industries; so that the want of such a school in this country, and the benefits which would accrue therefrom in manifold directions, could not but be recognised. In the autumn of that year Messrs. Gardner and Bullock induced the then Professor of Chemistry at the Royal Institution, Mr. W. T. Brande, to bring this prospectus before the managers, together with a carefully prepared scheme for establishing the scientific section of a British School of Practical Chemistry within the walls of the Royal Institution. In the preparation of this scheme, Messrs. Gardner and Bullock must evidently have had the assistance of Professor Brande, who appears to have been favourably impressed with the proposal.

The appointment of a Standing Committee of Management was

proposed, to consist of members of the Royal Institution and other men of science, of agriculturists, medical men, and of chemists and druggists. One of the earliest steps to be taken was to approach the Government through the Board of Trade, with the view of obtaining State aid. The fees to be charged to students were to be fixed at a very moderate amount, it being proposed to support the School by funds independent of those derived from fees. When these funds had been secured (to quote the scheme) the School was to be "established upon a broad basis"; the scientific section was to be capable of receiving 30 or 40 pupils; a Professor was to be appointed at a salary adequate to secure his undivided attention to the great purposes of the School; and it was considered that, if a thoroughly competent man were appointed from one of the great German Schools, a commencing salary of £250, with a liberal share of the students' fees, would offer sufficient inducement to secure the services of a man of acknowledged eminence.

The scheme proceeded to indicate that the premises in Albemarle Street were adequate to provide a capacious laboratory, where chemical science could be practically taught, and in which each student would have a separate working bench; the establishment was t include a private room and laboratory for the Professor, a balance room, an apparatus room, and store rooms. The plans for fitting up the laboratories were given in some detail. The scheme included the provision, apart from the scientific school, of a practical laboratory for the pursuit of studies on the most important applications of chemistry; this it was proposed should be placed under the direction of Mr. Lloyd Bullock, subject to the supervision of the Professor, and it was to be established in capacious apartments in George Street, Hanover Square (which became the temporary laboratory of the College in 1845). Mr. Bullock proposed to offer his services for the benefit of the practical school gratuitously. Lastly, it was considered that the provision, by subscriptions or grants, of an annual income of £800 to £1,000, would suffice for the maintenance of the School.

The managers of the Royal Institution referred this scheme, in November, 1843, to Professors Brande and Faraday, who reported favourably on the objects of the proposed School to the managers at their meeting on the 4th December, 1843. Messrs. Gardner and Bullock were therefore invited to attend to give explanations, and it was afterwards resolved that the subject be again referred to the Professors for a further report, which was presented by them on December 19th. In this report, after a brief discussion of the scheme, Messrs. Brande and Faraday stated that the existing laboratory in Albemarle Street, with the room and cellars beyond, would appear

to afford sufficient accommodation for the scientific school. The School of Chemistry (lectures) for medical students and others, conducted by Mr. Brande, would be thereby displaced, but, from consultation with Mr. Vulliamy, he was satisfied that accommodation for his courses could be provided in the Model Room, the models being transferred to the Battery Room. It appeared, therefore, "that place *could* be made for the School in the Royal Institution, but at a loss of many conveniences to itself and its Professors."

The words with which the report concludes illustrate in how thoroughly impartial a manner the eminent Professors of the Royal Institution dealt with a proposal which, if carried into effect, could not but have seriously interfered with their convenience and comfort in the pursuit of their work at Albemarle Street, and especially so in the case of that indefatigable investigator the resident Fullerian Professor of Chemistry. They say—

"The result of our consideration is strong approval of the end proposed, and a desire that it may be carried out in the Royal Institution if it can be done well. We venture to submit our impression in such a form to the managers that, if approved, the degree of approbation and assistance which the Royal Institution may be willing to give be expressed as follows:—

"Considering the great object of the advancement of chemical science and of good to the community contemplated by the establishment of the proposed School, and the perfectly disinterested intentions and views of its promoters and supporters, the Royal Institution is willing and anxious to aid such an object as far as it can, consistently with the rights and privileges of its members; and if hereafter the proposers are in possession of names of supporters and pecuniary means sufficient to carry out the objects proposed, the managers will on their part be prepared to recommend to the members of the Royal Institution the appropriation of apartments in the house for the purposes of a scientific laboratory for the proposed School."

The report of the Professors evidently received very careful and anxious consideration by the managers, and the subject was also exhaustively discussed in correspondence between the Secretary, the Rev. Mr. Barlow, and the President, Lord Prudhoe (afterwards Duke of Northumberland). Upon a resumption of the discussion on the report, the week following its presentation, Professors Brande and Faraday informed the managers that after a closer examination of the limited space within the walls of the Royal Institution, and a careful consideration of the room required for the great and increasing stock of apparatus, minerals, and books, it appeared to them impracticable to afford accommodation to the proposed School,

whereupon the managers requested the Secretary to intimate to Messrs. Gardner and Bullock their regret that the space at their disposal was too limited to justify them in acceding to their request.*

The indefatigable promoters of the scheme for the establishment of the British School of Practical Chemistry did not relax their exertions after the failure of their negotiations with the Royal Institution, and continued to secure important accessions to the list of its supporters. At a public meeting held at the temporary offices of the College of Chemistry in St. Martin's Place, on the 29th July, 1845, a definite form was given to the proposed Institution, and, after the election of a Council and certain executive officers, the first, all-important, subject which received anxious consideration was the appointment of a Professor. One of the earliest and most prominent supporters of the movement was the amiable and accomplished Physician in Ordinary to the Queen, Sir James Clark, Bart., who became at the outset one of the staunchest and most active workers in the interests of the College of Chemistry, and an invaluable friend of the first Professor, and who was soon afterwards associated in both capacities with the Hon. William Bingham Baring, afterwards Lord Ashburton.

In Hofmann's interesting *Page of Scientific History* he points out that there was at that time no lack of most excellent chemical lecturers in England, and that, indeed, the style of experimental lecture-illustrations in general use in England was greatly superior to that which then prevailed in Germany and other parts of the Continent; but that the greatest want felt was easily accessible, efficient instruction, not only in systematic chemical analysis, but also in methods of conducting experimental inquiry, and it was with a view to meet this want that it was decided to follow the counsel of Sir James Clark, and apply to Liebig to select a suitable man from among his own assistants or past pupils for the appointment of Professor to the new College.

The story of the circumstances which secured the services of Hofmann for the foundation and development of the College are graphically narrated by himself in his *Page of Scientific History*. The refusal of the appointment successively by Fresenius, then already Professor at Wiesbaden, and by Will, Assistant Professor at Giessen, and the desire of Hofmann, at that time "Privat Docent" at Bonn, to accept it, mingled with the natural hesitation

* Since this was read to the Chemical Society, in May, 1893, the proposal favoured by Professors Brande and Faraday has been thoroughly realised, through the munificence of Mr. Ludwig Mond, by the establishment of the "Davy-Faraday Research Laboratory," adjoining the Royal Institution, and under the direction of its managers.—F. A. A.

to risk, through the occupation of a possibly precarious position, the serious interruption of a bright career just commenced at the Rhenish University; the happy solution of the difficulty through the gracious and invaluable intervention, at the instigation of Sir James Clark, of the late Prince Consort, who had from the first taken a warm interest in the proposed establishment of the English Chemical College, and who happened to be staying with the Queen at Brühl when the negotiations were proceeding; the appointment of Hofmann as Extraordinary Professor at Bonn, accompanied by an immediate grant of two years' leave of absence, so that he might at once re-enter upon his career in Germany should the English enterprise fail; his speedy departure for England, and the commencement of operations in the temporary laboratories of the College of Chemistry in George Street, Hanover Square, in October, 1845: all these incidents in the early history of the College have been recounted in interesting detail by Hofmann himself and by his pupil and brother-in-law, Dr. Tiemann.

For the first session, 26 students had entered, and among these were Warren de la Rue, F. A. Abel, E. C. Nicholson, Henry How, Thomas Rowney, C. L. Bloxam, and Robert Galloway. The laboratories in George Street were fitted up in temporary and very economical fashion, and I well remember the energetic way in which Hofmann set to work immediately upon his arrival in London, aided by the amiable young Herman Bleibtreu, whom he had brought with him as a temporary assistant, and whose quaint semi-military attire and imperfect English were a little trying to the powers of control of some among the younger students of the first session.

Hofmann's complete sway over his pupils was at once secured by his indomitable perseverance and inexhaustible patience with the dullest, his earnestness of manner—his clearness of exposition, rendered additionally attractive by an inherent quaintness and a power of happily rendering German expressions into graphic English. Those first two sessions of the College, in the scantily equipped laboratories, with makeshift contrivances of the crudest character, and an utter absence of any convenience for conducting investigations, must have been a sore trial of patience and powers of endurance to the impetuous young teacher, and to the enthusiastic worker, whose only recreation was the pursuit of original research. When to these circumstances is added the mental strain involved in the almost continuous pursuit of instruction and discussion in a foreign language for at least eight hours daily, to say nothing of continued anxious consultations with the Council and officials of the College regarding ways and means; the heavy work connected with the erection and equipment of the permanent laboratories; the grappling

with the problems of maintaining and fostering public interest in the Institution, and of keeping current expenses within very moderate bounds,—it is self-evident that no small moral courage and powers of endurance were needed for the successful accomplishment of these duties, and for the maintenance of the confident and apparently light-hearted demeanour, and of the power of instilling into others confidence of future success, which were peculiarly characteristic of Hofmann in those days of supreme difficulty. But these very characteristics, added to his genial and charming manner, high flow of spirits, and originality in conversation and correspondence, secured to him devoted friends, not merely among colleagues and pupils, but in whichever direction social intercourse was opened up to him. Just as his earnestness of purpose and enthusiasm kindled corresponding qualities in a large proportion of his pupils, so also his sanguine temperament and airy treatment of difficulties maintained, among many of the early friends and important patrons of the struggling Institution, a steadfastness of purpose which otherwise would doubtless have speedily waned.

Among the most prominent of the first students at the College, there was one who at once exercised a very marked beneficial influence in establishing a spirit of emulation, combined with good fellowship, among the younger students, and who speedily became one of Hofmann's most intimate and most useful friends; it is almost needless to say that I refer to Warren de la Rue. A bright example to all in industry and unflinching perseverance, manipulative skill, and methodical work; of calm courage and presence of mind in the face of sudden emergencies such as are bound to arise occasionally in laboratories where a great variety of experimental work is in progress; the embodiment of amiability, ever ready to lend a helping hand, in whatever direction it might be needed; now acting as sagacious adviser in difficulties; now as arbitrator in disputes or differences which would occasionally arise between fellow students; always active in the interests of the school;—no man could have made himself more universally beloved than De la Rue. There can be no doubt that he laboured as importantly, as he did unobtrusively, for the good of the College in the days of its greatest troubles, and was a powerful support to the Professor in *his* constant battles against formidable difficulties with which, suddenly launched as he had been upon a new career in a strange land, he would indeed have found it much harder to grapple successfully, in the absence of two such trusty friends and able supporters as Sir James Clark and Warren de la Rue.

There is but one opinion among those who can appreciate the stupendous difficulty of the task so brilliantly accomplished by Hofmann, in placing the College of Chemistry upon a sure foundation,

and in securing to it, within a very few years, a high position among the chemical schools of Europe;—that his success was ascribable to the possession of a happy and rare combination of the highest talents as a teacher with exceptional powers as an investigator, inexhaustible industry and energy, and an enthusiasm not to be subdued by any obstacles; a characteristic quality possessed in the highest degree by his great master, Liebig.

It was Hofmann's rule, to which, during the continuance of my stay at the College he strictly adhered, to visit each individual student twice during the day's work, and to devote himself as patiently to the drudgery of instructing the beginner, or of helping on the dull scholar, as he did, delightedly, to the guidance of the advanced student, whom he would skilfully delude into the belief that the logical succession of steps, in making the first investigation which the master had selected for pursuit by the pupil, was the result of skill in research which he had already attained, instead of being simply or mainly the skilful promptings of the great master of original research.

It was not until the work of the College had been well established in the new laboratories in Oxford Street that Hofmann began to give courses of lectures; but even in the first session he would occasionally deliver, at the bench of a particular pupil, short expositions of certain subjects, addressed to the body of the students in the laboratory, which were very attractive in style and matter, and always listened to with great attention.

In some interesting notes about Hofmann, which have been very kindly shown to me by Professor McLeod, who was his favourite lecture-assistant some considerable time after I had quitted the College, he testifies to the remarkable knowledge of English, and powers of expression therein, possessed by Hofmann; to the attractiveness of his manner, and to the way in which he carried his audience with him by his enthusiasm; so that his great tendency to exceed, and somewhat considerably, the usual hour, never gave rise to impatience or fatigue with the young students. He devoted much time to the suggestion or contrivance of lecture illustrations, and was very particular in having his discourses appropriately, but not profusely, illustrated by experiments.

To return to the early days of the College: its promoters having succeeded in securing premises in Hanover Square suitable for official and residential purposes, with an open space in the rear, facing Oxford Street, plans for a set of commodious laboratories were speedily prepared under Hofmann's guidance and with valuable aid from Warren de la Rue, and the first stone of the building having been laid by the Prince Consort on the 16th June, 1846, the third session of the College was actually commenced in the new labora-

tories in October of that year. In the second session, beginning in March, 1846, 37 fresh students had entered, making 63 in all, and the two small temporary laboratories in George Street became inconveniently crowded. Among the new men were the much-beloved and lamented Charles Mansfield, whose terrible death affected Hofman deeply; Frederick Field, Poet Laureate of the College, who became one of Hofmann's favourite pupils; George Merck, of Darmstadt; Henry M. Noad, and Bransby Cooper—all, long since, passed away. At the beginning of this session I was appointed by the Professor to help Dr. Bleibtreu, and afterwards Dr. Blyth, in the work of elementary instruction, and of maintaining the equipment of the temporary laboratories, and, towards the close of that session, two of my fellow students (dear friends of mine, whom their master long outlived) were selected by the Professor for similar posts of honour and hard work; Edward Chambers Nicholson, and the comparatively very youthful pupil Charles Loudon Bloxam; the first possessed of veritable genius as a *preparateur* (having already acquired some considerable skill during a brief apprenticeship in the business of Mr. Lloyd Bullock); the second, exhibiting at the very outset a marked predilection and talent for tutorial work.

A highly busy time we three young fellows had of it during the summer vacation of 1846, in the back kitchen and scullery of the house in Hanover Square (the George Street laboratories being in course of dismantlement), preparing the material for stocking the sets of reagent-bottles for over 60 students; finding time also for a little special experimental work. Thus, Schönbein having then recently published his instructions for the production of gun-cotton, I prepared a somewhat considerable quantity of that material (little dreaming that, 15 years later, I should begin to become in some measure identified with it); and the small remnant which I have still preserved of that preparation, bears witness to the care with which its purification was accomplished and consequent stability secured by the young student. Our activity in the basement of the College premises in Hanover Square during the summer and autumn of 1846 must, however, have been less to the taste of the immediate neighbours than to ourselves and our Professor, for, in the minute-book of the College Council, is recorded a resolution, dated October of that year, directing the immediate removal of all chemicals and laboratory operations from the kitchen and other apartments into the laboratory.

The new establishment in Oxford Street included a small private laboratory for the Professor, and, before the close of the year, Nicholson was already busily engaged therein upon the work of research which Hofmann at once resumed with an ardour intensified

by the compulsory abstention from the delight of his life—to which he had been compelled for a time to submit. The first investigation upon which Nicholson had to work was on the action of cyanogen on aniline, toluidine, and cumidine, while he, at the same time, carried out, under Hofmann's direction, his own first investigation on the compounds of phosphoric acid and aniline. *My* time was divided between the duties of teaching, which I shared with Bloxam as my junior (for a time under that most amiable and painstaking teacher, Dr. John Blyth, who had been appointed Assistant-Professor), and the work of another branch of Hofmann's prolific aniline researches, viz., the investigation of the action of chloride of cyanogen and bromide and iodide of cyanogen upon aniline (from the effects of which my eyes suffered permanently). At the same time, I also carried out my first organic investigation and the analysis of the mineral waters of Cheltenham. In the latter and other analytical research work I became associated with another fellow-student, Thomas H. Rowney, whom Hofmann appointed as his first lecture-assistant.

It is difficult to estimate the full value, to the individual concerned, of the severe work, and the many-sided training, which an assistant of Hofmann experienced, more especially in those earliest days in the history of the College of Chemistry. Dr. Tiemann quotes from important materials for a biography of Hofmann which Dr. Max Kopp has prepared, the following words of the latter in referring to some of his former master's earlier stupendous investigations:—"Thank God, what cause we have to admire, besides our master, the patience and powers of endurance of the assistants of those days;" and certainly the work which we then accomplished in the arduous but happy life we led was well worthy to be called hard work. As an illustration, I venture to sketch, in a few words, the routine which for five years I pursued as assistant at the College of Chemistry. A walk of about five miles brought me to the College before nine, the students' hours being from nine to five. The work of teaching, and attention to the requirements of the students, then went on continuously, simultaneously with the conduct of research work, and with the incidental production of materials for that work. One-half of my table in the principal laboratory was devoted to the operations connected with the Professor's investigations; the other half to my own researches. Ever and anon a student would come for assistance and advice, which led to my experimental work being of a somewhat perplexingly intermittent character. Hofmann began his first round among the students at half-past nine, and, having completed this, he divided his attention between the research work in Nicholson's hands and that with which

I was entrusted. A roll and butter or some biscuits, devoured while work was going on, constituted my midday meal, and I reached home at half-past six, frequently returning to the laboratory in the evening to carry out combustions (which Nicholson and I learned to do in couples, with charcoal fires, be it remembered) or other special operations, or to work out results, discuss them and prepare papers, with the Professor, or to make some progress with my own investigations, returning home late at night. When not thus employed, the evenings were devoted to the coaching of students, at from three to five shillings the hour, or to literary work, such as the translation of the *Jahresberichte* of Liebig and Kopp, for its English editors, Hofmann and De la Rue, so as to supplement the magnificent income of £40 a year, upon which we assistants were "passing rich." One evening weekly we had a students' meeting for papers and discussions, which Hofmann used to make a point of attending and taking part in. When the two months' vacation-time came round, we assistants used to take, at the most, a fortnight, for there was much to be done to prepare the laboratories for the next session's work; and, before his departure for his well-earned holiday in Germany, the Professor left his assistants a liberal allowance of work to be performed by his return: such as the preparation of a supply of aniline from indigo, the development of new methods for the production of materials for his researches, the analyses of new products, or the construction of special apparatus. But the life, although somewhat arduous, was a thoroughly happy one; *who* would not work, and even slave, for Hofmann? It was a rich reward to receive a word of commendation of a skilfully constructed piece of apparatus (for in those days very much had to be accomplished with tubes and corks and sheets of india-rubber); or to hear an expression of contentment at a successful distillation for aniline (the production of a few ounces being a proud achievement); or the attainment of a good instalment of analytical results. Hofmann highly appreciated skilful work; manipulative dexterity being his weak point (he used to tell us that, in his student's days, all his fingers were thumbs, and that he could hardly handle a test tube without "scrunching" it). There was an indescribable charm in working with Hofmann; in watching his delight at a new result, or a successful operation; or his pathetic momentary depression when failure attended the attempt to attain a result which theory indicated. "Another dream is gone," he would mutter plaintively, with a deep sigh; but not for long was he despondent. "Never mind," he would soon exclaim, "we shall have it to-morrow!" His inherent buoyancy of spirits helped him through all trials, of which those relating to official and personal concerns, or domestic sorrows, of

which he experienced many in quick succession, were apparently as nothing compared with the failure, for the time, to achieve the result which his sagacity predicted, and which sooner or later he attained.

The students who, during my career at the College, which terminated early in 1851, were advanced by Hofmann to the post of Assistant, partly to help with the general work of instruction and to prepare and assist at his lectures, and partly to work at his researches, were Abel, Nicholson, Bloxam, Rowney, Brazier, and Medlock; several of my colleagues left soon after my departure, and the subsequent roll of student-assistants included many names since well known in the scientific world, and many old Fellows of the Chemical Society: Crookes, Spiller, Tookey, Reginald Morley, J. S. Abel, Ansell, Church, Matthew Johnson, H. M. Witt, McLeod, Groves, Valentin, Barrett, Bassett, Vacher, O'Sullivan, and Reynolds; and the private assistants, who were exclusively employed upon his researches, embraced a succession of well-known German names, of which several have become famous: P. W. Hofmann, Fischer, Fries, Bopp, Griess, Förster, Ulrich, Martius, Olshausen, Willbrand, Sell, and Geyger.

When the Assistant-Professor, Dr. Blyth, left the College to become Professor at Queen's College, Cork, an old fellow-student of Hofmann's, Sheridan Muspratt, occupied for a short time the post of Honorary Assistant-Professor, and another Giessen student of more recent date, Dr. David S. Price, was also for a time an Honorary Assistant at the College.

There can be no doubt that one of Hofmann's talents which most importantly contributed to his eminence as an industrious and successful investigator, was his faculty of gauging the powers and special qualifications of those who studied under him; it enabled him to select the fittest workers to aid him in the rapid and successful development of a great diversity of researches, and also to direct their special talents and energies into channels which his prolific mind suggested, and the exploration of which, by those whose powers he, in the first instance, discovered and fostered, laid the foundation to the practical usefulness, or the scientific eminence, which many have attained who are now glad and proud to remember that they were the pupils of Hofmann.

A glance at the contents of two volumes published in 1849 and 1853, entitled *Reports of the Royal College of Chemistry and Researches conducted in the Laboratories*, affords interesting illustrations of the manifold directions in which Hofmann guided the students to whom he opened up the inexhaustible fields of original research, and of the fertility of mind which, while he himself was conducting simul-

taneously several investigations, continually branching off into new ramifications, enabled him to suggest a multitude of fresh subjects for work to his students—many of which developed into researches of considerable importance—and to hold the guiding strings of all firmly within his grasp.

Mindful of the importance, to the struggling Institute of which he was the head, of enlisting and maintaining the interest of representatives of professions, industries, commerce, and of landed property, in its work, and of fostering faith in its utility, he encouraged advanced students of a mechanical turn of mind to undertake analyses of waters, soils, ashes of plants, minerals or alloys, or to seek to improve existing, or devise new, analytical methods, or new forms of apparatus; but there is no question that he best loved to place in the hands of his most capable pupils one or other of the many problems in organic chemistry in the solution of which he took a paramount interest. Hofmann's assistants well remember an inseparable pocket companion of his; a small memorandum book, in which he kept a numbered series of subjects for research, and to which additions were frequently made; from these he selected, from time to time, the subject which he placed in the hands of a sufficiently advanced pupil for investigation.

The two volumes to which I have referred record the original papers published during the first five years of the College's existence; they embrace 21 researches in organic chemistry by 19 different pupils, and 15 analytical and other papers in inorganic chemistry by 14 different pupils. But they also include a series of nine of Hofmann's earlier memoirs on the volatile organic bases, besides other researches of much interest conducted by him during those five years of ceaseless activity. In the two or three years following, the number and importance of published memoirs emanating from the College of Chemistry was at any rate maintained, and some valuable technical investigations were, in addition, carried out by Hofmann in conjunction with Professors Graham, Miller, and Redwood.

I have already referred to Hofmann's intimate knowledge of English, even in the first days of his advent here, and of the immediate success which was secured by his lucidity of exposition, even although many of his expressions were at first somewhat literal renderings of his German thoughts. His mastery of the language was extremely rapid, as was testified by the success of two or three most interesting lectures which he delivered to general audiences (subscribers to the College) within two years of his appointment, and by the "Remarks on Experimental Science" and "Introduction to Researches," which constitute the charming and most suggestive prefaces to the first volume of the researches conducted in the laboratory of the College,

and were written between three and four years after his arrival in England. No one could doubt, who *saw* him and listened to him, when lecturing or taking part in a discussion, that he thoroughly enjoyed public speaking, and no one was followed with closer attention, or with greater interest and enjoyment, than Hofmann when giving the substance of a new research, or taking part in a discussion at this Society's meetings. It cannot be denied that he was somewhat vain of his English; thus, in going through papers prepared by his English students for publication, he did not confine his criticisms to the matter of the treatise, but would not hesitate to alter the language in conformity with his view as to the correctness or appropriateness of expressions or composition. In the preparation of his many memoirs, reports, and addresses he was extremely painstaking, and such truly classical treatises as his discourse "On Ammonia and its Derivatives," published in the *Journal of the Chemical Society* in 1858, and his report on "Chemical Products and Processes," prepared in connection with the International Exhibition of 1862, are monumental illustrations of the thoroughness of his writings. His speeches on festive occasions were a source of much interest to the listeners and of pleasure to himself. The reference to the Exhibition of 1862 recalls to my mind the happy speeches which he delivered in French, German, English, and Italian, when presiding over an entertainment given at Greenwich to the foreign members of the juries, and some there are here present, though, alas! the ranks have been terribly thinned, of his old pupils who will vividly recall to mind that splendid speech in which he bade farewell to them on the occasion of the parting banquet given to him in 1865 by the majority of those who had worked under him at the College of Chemistry.

His famous orations in German, on two recent memorable occasions at Munich and Göttingen, are still fresh in the memory of his many friends here and abroad; but among his many memorable addresses there is one which is invested with a special pathetic interest—the affecting memorial speech which he delivered at the German Chemical Society on the death of his much-loved friend and fellow student, Hermann Kopp, who succumbed to a long and painful illness but a few weeks before Hofmann was so suddenly called away.

Hofmann's life should, and must, have been a very happy one, even although it was often clouded by domestic calamity. He attained to honours and dignity which were tokens of full official and public recognition of his high merits and of valuable services rendered to science and the State. Ample resources and a vigorous constitution enabled him to devote to the great pursuit of his life—research—the little leisure his professorial, literary, and official duties left him. Moreover, he possessed in the highest degree the faculty of making

friends. To be his pupil was to become attached to him—the patient teacher, the enthusiastic worker, the cheering and brilliant companion, to whom it was a pride and pleasure to render service; he readily made and bound to himself powerful and influential friends, and was cordially welcomed wherever he went. He was treated with much kindness by the Queen, and by the Prince Consort who paid repeated visits to the laboratories of the College of Chemistry; he several times delivered lectures at Windsor Castle. Upon his appointment at Berlin he was at once most graciously received by the then Crown Princess of Prussia, the Empress Frederick of Germany, who recently spoke to me of her great sorrow at the death of her dear master and friend, as she called him, and of her high admiration of his talents and character.

The ease with which Hofmann made friends at the very outset of his London career, and the rapidity with which he adapted himself to English customs and mode of life, combined to speedily make him thoroughly at home here, and strongly attached to England and the English. Even after his return to Germany he was fond of speaking of England as his adopted country, and I remember in 1849, when replying to my inquiry whether he had enjoyed his summer vacation in Germany, his saying that he never felt thoroughly at home until he once more trod the London pavement.

The following passages from a charmingly worded German letter, addressed by Hofmann to the Prince of Wales, who, as President of the Society of Arts, wrote to him in 1882, congratulating him upon being the recipient of the Albert Medal, illustrate the pleasure with which, whenever occasion offered, he referred to his career in London.

"The gracious words of your Royal Highness carry me back to the most charming period of my youth—to the time when the August Father of your Royal Highness, the ever memorable Prince Consort, exercised a most important influence upon my destiny—as he did upon those of many—by determining the direction of my future life. I shall never cease to be thankful for the fortunate combination of circumstances whereby I was brought into contact with the high-minded Prince, whose active sympathy opened up to me, at a comparatively early period of my life, a sphere of action in the English metropolis, replete with stimulation and instruction, such as never could have been secured to me by my personal exertions.

"Your Royal Highness will therefore appreciate the depth of feeling with which I receive from the hands of the Son, the medal founded in memory of the Father, and the profound emotion with which I gaze upon the faithful reproduction of the noble features of the so-early

departed one, to whom I, in reality, am indebted for the honour now bestowed upon me.

"With the assurance that the Albert Medal and the letter of your Royal Highness which accompanied it will be inherited by my family as an inseparable legacy,

"I am, Sir,

"Your faithful servant,

"A. W. Hofmann."

I have endeavoured in this notice to present to the Fellows of the Chemical Society some details of interest relating to the foundation and early history of the School of Chemistry with which the name of Hofmann is identified, and to pourtray some characteristics of this eminent chemist, more especially in the capacity of teacher.

With the nature of the multifarious invaluable research work which he has accomplished I have not ventured to deal in any way; the interesting task of reviewing that work is in much abler hands than mine—in the hands of one of Hofmann's most distinguished pupils, of whose achievements he has often spoken and written in glowing terms; whom I envy the splendid work he himself has accomplished and is still pursuing with undiminished ardour; and who, free from the trammels of official life, has been able to keep pace with, and continue intimately concerned in, the rapid strides which chemical science has made since, half a century ago, the cultivation of that science became a branch of national education in this Country through the invaluable combination of circumstances which placed England under a lasting debt of gratitude to August Wilhelm von Hofmann.

The Origin of the Coal-Tar Colour Industry, and the Contributions of Hofmann and his Pupils.

By W. H. Perkin, Ph.D., D.C.L., F.R.S.

The illustrious man whose lifework we are called on to commemorate, was well known to very many of us, especially those who had the privilege of being his students and assistants. We can all recall the pleasure and interest with which we listened to the lucid and graphic accounts of his researches which he used to bring before the Chemical Society in years gone by; and great was felt to be the loss not only to us, but also to the country, when he left it for his fatherland: but now we mourn a far greater loss, and one which we realise more and more deeply as we consider the incidents of his remarkable career—a career of such incessant activity and brilliant achievement.

I am charged with a duty which I wish had been placed in more capable hands than mine: to give an account of the rise and progress of the coal-tar colour industry, and its relation to the Hofmann school; and, as being connected with its commencement, I am requested to make the account to a large extent autobiographical—a part of my task which it would have been more agreeable to me to have seen undertaken by others rather than myself.

This industry holds an unique position in the history of chemical industries, as it was entirely the outcome of scientific research. We have to go back to 1825, when Faraday discovered benzene, or, as he then termed it ,, bicarburetted hydrogen," for the first investigation which clearly bears upon the subject. Faraday separated the hydrocarbon from the liquid products condensed on compressing the gas obtained from oil. A year later (1826), Unverdorben obtained aniline by the mere distillation of indigo, and called it "crystalline." Runge afterwards obtained it from coal-tar oil, and having observed that it produced a violet-blue coloration with chloride of lime, called it "kyanol." It was subsequently obtained from indigo by Fritsche by distilling this colouring matter with caustic alkali. We then come to the important work of Mitscherlich, who obtained the hydrocarbon benzene from a new source, namely, benzoic acid,—whence the name, and produced from this nitrobenzene. Zinin subsequently found that *benzidam*, as he termed it, could be produced by the action of sulphuretted hydrogen in presence of ammonia on an alcoholic solution of nitrobenzene.

This brings us to the commencement of Hofmann's researches on aniline, a substance which he used sometimes to speak of as his "first love." In his first published paper he showed that Unverdorben's crystalline, Runge's kyanol, Fritsche's aniline, and Zinin's benzidam were all the same compound, for which he afterwards selected Fritsche's name, aniline. Later on, Hofmann and Muspratt prepared toluidine from toluene from tolu balsam.

The work on the separation of aniline from tar was done before the date of Hofmann's coming to this country, viz., in 1843. After his arrival here in 1845, he continued his researches, and, to realise something of his indomitable perseverance, it is necessary to remember that, until the coal-tar colour industry was established, practically all the aniline he used in his numerous enquiries was procured by the laborious and costly process of distilling indigo with potash.

In 1843, organic chemistry was still in its infancy, and coal-tar naphtha had not yet been investigated. Runge had isolated carbolic acid, pyrrol, kyanol or aniline, and leucol or quinoline. Naphthalene was well known to exist in tar, having been separated by

Garden, as early as 1820. Dumas had discovered paranaphthalene or anthracene, and chrysene and pyrene had been referred to by Laurent, but these were very doubtful compounds. This was about all that was known of the composition of coal-tar at that time. Hofmann showed, in 1845, that benzene must exist in the naphtha, as he found that aniline could be produced from it, but he never separated this hydrocarbon; shortly afterwards, however, he induced his pupil, Charles Mansfield—of whom he always spoke in the highest terms—to undertake the investigation of the liquid hydrocarbons of coal-tar.

On reading over the account of Mansfield's investigation, and bearing in mind that in those days fractional distillation was conducted in old fashioned glass retorts with the thermometer in the liquid, it is impossible not to admire the patience and perseverance he exercised, as well as the systematic and skilful manner in which he worked.

All who have undertaken fractional distillations, even with all our present knowledge and improved apparatus, know how difficult it is to detect and isolate products in a mixture such as coal-tar naphtha. Yet Mansfield obtained benzene in a pure state, and toluene sufficiently so for Hofmann to prepare toluidine from it. He also obtained pseudocumene, and was led to believe in the existence of xylene. In describing his work, he modestly remarks:—

"It has been perhaps the tedium of the methods necessary to effect a separation of mixed hydrocarbons from each other, which has deterred experienced chemists from devoting their time to disentangling the oils here treated of: and perhaps to have conducted the innumerable distillations necessary for this purpose in a laboratory imperfectly furnished with gas and other conveniences, would have been a task too laborious to have been persisted in." (*J. Chem. Soc.*, 1849, **1**, 246.)

Amongst the enquiries carried on by Hofmann, in the early days of the Royal College of Chemistry, were those classical "researches regarding the molecular constitution of the volatile organic bases," in which he succeeded in displacing the hydrogen of the NH_2-group by different alcohol radicles, eventually obtaining also the ammonium compounds. In the first of these (*J. Chem. Soc.*, **3**, 1851) he describes ethylaniline (p. 284), and diethylaniline (p. 288), also methylaniline (p. 295). The method used in these researches, of substituting hydrogen in amines by means of the iodides and bromides of the alcohol radicles, and also the substituted anilines which were obtained, although not connected with the foundation of the coal-tar colour industry, have been of great value in its after development. These few references to observations on the early work carried on at the Royal College of Chemistry, for the sake of science *only*, show, in fact, what valuable material was produced for

the coming new industry; indeed, without the research of Mansfield, it could never have become an industry.

The foregoing brings the work of the Royal College of Chemistry up to near the date when I became a student there, and it will, perhaps, be well if I here refer to my young days, and state how it came to pass that I had the good fortune to study under Hofmann, especially as it will enable me to say a few words in reference to one of his old pupils who has done much for the cause of science.

As long ago as I can remember, the question what pursuit I should follow was constantly before me. Even when very young, I interested myself in several subjects of a mechanical kind, and worked at them to the best of my ability; and elementary as the experience then gained was, it had a lasting influence upon me. When I was between 12 and 13 years of age, a young friend was good enough to show me some chemical experiments; amongst these were some on crystallisation, which seemed to me most marvellous phenomena: as a result, my choice was fixed, and it became my desire to be a chemist, if possible, as I saw that there was in this science something far beyond the mechanical and other pursuits I had been previously occupied with. At this time I left the school I was attending, and entered the City of London School, of which Dr. Mortimer was then head master. Here lectures were given on chemistry and natural philosophy; indeed, I believe this was the first school in which experimental science was taught. The lecturer was one of the masters, Mr. Thomas Hall, B.A. (Lond.), an old sudent of Hofmann's, who had obtained all the chemical knowledge he possessed by working at the Royal College of Chemistry. To attend these lectures was a source of great pleasure to me. There was also a yearly examination in science, and the examiner was also one of Hofmann's pupils, and his first assistant, none other than my friend Mr., now Sir, Frederick Abel. In the City of London School I was consequently brought directly under Hofmannic influence, if I may so term it, for all who came in contact with those who worked with him had infused into them by induction his enthusiasm for chemistry. Mr. Hall very soon took an interest in me, and installed me as one of his lecture assistants. Science, however, was not allowed to interfere with the ordinary school curriculum, so that the lectures, and the preparations for them, were delegated to the interval for dinner, and being very much interested in preparing the experiments, I not unfrequently found this interval had passed before I had left off work; but, fortunately, I never found that the abstinence thus caused acted prejudicially upon me. Whilst with Mr. Hall, I heard much of the Royal College of Chemistry and its Professor, and after my master had very kindly had several interviews with my father—who wished me to be an architect and not a

chemist—it was my good fortune to be allowed to follow my bent, and go to the Royal College of Chemistry, in Oxford Street.

Before passing from my schooldays, I feel I must say a few more words about my old school-master, to whose kindness I owe so much. Thomas Hall was a born teacher, who took an individual interest in his scholars, studying their characters, and stimulating any special qualities he saw they possessed, and, at the same time, inculcating the highest moral qualities. He hated anything that was mean or underhand, and, at the same time, was very genial and kind-hearted; this may be gathered from the fact that the boys used to speak of him as *Tommy Hall*. His influence on behalf of science, especially the science of chemistry, was great; it appears, from a list of old City of London School boys, kindly given me by Mr. John Spiller, that more than 30 boys in whom he had taken an interest afterwards worked at the Royal College of Chemistry, and of these I may mention the following as having contributed papers to our Transactions:

J. J. Bowrey, J. T. Brown, Frank Clowes, W. H. Deering, Edward Divers, J. A. Newlands, F. J. M. Page, W. H. Perkin, Alexander Pedler, J. Spiller, and W. Thorp.

I entered the Royal College of Chemistry when I was in my fifteenth year, at the time when that institution became part of the School of Mines, but I only took up the study of chemistry. After seeing Dr. Hofmann with my father, the first person I encountered in the laboratory was the Assistant, Mr. W. Crookes, who set me to study the reactions of the metals.

There was no theatre at the Royal College then, and the students had to go to the Museum of Practical Geology in Jermyn Street to hear the lectures on chemistry, which involved a rather serious loss of time; but the lectures made up for this, as Hofmann spared no pains in making them as interesting, instructive, and perfect as he possibly could, illustrating, as far as practicable, everything by experiment, so that the facts were firmly impressed upon the mind At that time he also had a very efficient lecture assistant, the late Mr. Witt. Hofmann was good enough to let me attend these lectures a second time.

When going through the ordinary course of qualitative and quantitative analysis, the students working at research appeared to me to be superior beings, something beyond ordinary persons; and being possessed with a desire to join their ranks, the ordinary course, and also gas analysis by Bunsen's method, was quickly gone through. Hofmann then set me to work at research, and very curiously gave me as a subject the hydrocarbon anthracene, or, as it was generally called in those days, paranaphthalene. To obtain this, pitch was taken as the starting point, but as it was found that this method of

preparation was a very tedious one to carry out in the laboratory, Hofmann kindly obtained some of the crude product for me from Mr. Cliff, of Bethels Tar Works. As is well known, Hofmann—especially at that period—was much interested in the formation of organic bases from hydrocarbons, and the object of my investigation was to produce, if possible, a nitro-compound, and then convert this into a base by reduction. However, anthracene refused to give a nitro-compound, and consequently no base could be obtained, but, in the course of my work, I prepared the compound we now know as anthraquinone, and also the chlorine and bromine derivatives of anthracene. But these substances could not be got to yield intelligible results on analysis, and at that time it never occurred either to Hofmann or myself that there was any likelihood of Dumas and Laurent's formulæ for the hydrocarbon (*i.e.*, $C_{15}H_{12}$) being incorrect. The consequence was that this research was set aside, but I shall show further on that the experience I then gained was of great importance to me several years later, when I commenced to work at the production of alizarin.

Hofmann next set me to work to study the action of chloride of cyanogen on naphthylamine in the same way that he had examined the action of this gas on aniline. In those days there were no depôts where pure products for research could be obtained as there now are, and for this inquiry even the naphthalene had to be purified in the laboratory; this research was soon completed, but was not written out and published until nearly 12 months afterwards. It was brought before this Society when the meetings were held in Mr. Pepper's house in Cavendish Square.

Hofmann had a marvellous power of stimulating his students, and of imparting to them his own enthusiasm; he took the strongest personal interest in their work, visiting three or four times in the week even those who were going through the reactions, while those engaged in research work were seen daily by him, and if anything of special interest was going on, more than once in the day. His power of directing research was also most remarkable; with the aid of a few watch glasses, a glass rod, and a small gas flame he would make a number of experiments, and from the information thus gained tell his students how to proceed with their work. I well remember how one day, when the work was going on very satisfactorily with most of us and several new products had been obtained, he came up and commenced examining a product of the nitration of phenol one of the students had obtained by steam distillation; taking a little of the substance in a watch glass, he treated it with caustic alkali, and at once obtained a beautiful scarlet salt of what we now know to be orthonitrophenol. Several of us were standing by at the time, and,

looking up at us in his characteristic and enthusiastic way, he at once exclaimed, "Gentlemen, new bodies are *floating* in the air." I mention this just as an example of the way in which he used to stimulate us by his own example.

After I had completed the research on the action of chloride of cyanogen on naphthylamine, Hofmann promoted me to the position of an assistant in his research laboratory; I was then 17 years of age. Mr. A. H. Church, now Professor Church, was among the assistants in the laboratory. This position proved most valuable to me.

At this time Professor Cahours came over from Paris to work with Hofmann on the allyl compounds, a research in which Professor Church and I had to assist. They then commenced their splendid work on the phosphorus bases, and I well remember the excitement and interest which prevailed when Paul Thénard's triethylphosphine was first produced by the action of zinc ethyl on phosphorus trichloride, and Hofmann's delight when he found it was vigorously acted on by methyl and also ethyl iodide, producing white, crystalline, phosphonium iodides. I was occupied with this research until I left the Royal College.

I may here refer to an incident which shows how greatly Hofmann was interested in his scientific work. One day, when he was going his usual rounds in the general laboratory, a student standing not far from him poured a quantity of concentrated sulphuric acid into a thick glass bottle he was holding in his hand, which contained a small quantity of water; the consequence was that the heat evolved caused it to crack and the bottom to fall out. Some of the acid splashed up from the floor into Hofmann's eye, and we feared would have a permanently injurious effect upon it. Hofmann was sent home in a cab, and had to be kept in bed in a dark room during several weeks, his old friend, Dr. Bence Jones, attending him. But during this time, and notwithstanding his sufferings, he was so anxious about his work that we used to have to visit him in his darkened bedroom, to report progress and also to receive any instructions he had to give.

Whilst in the research laboratory I had the privilege of meeting St. Claire Deville, who came to London for the purpose of exhibiting specimens of sodium and aluminium at a lecture given by the Rev. T. Barlow at the Royal Institution, of which the lecturer was Secretary.

Whilst assistant under Hofmann, I had but little time for private work in the daytime; as, however, I wished to continue research work, part of a room at home was fitted up as a rough laboratory, and there I was able to work in the evenings or during vacations.

In this laboratory a research was carried on conjointly with Mr. Church on some colouring matters derived from dinitrobenzene and dinitronaphthalene. One of the products we then obtained afterwards proved to be amidoazonaphthalene, or, as we called it, azodinaphthyldiamine. This appears to have been the first case of a definite compound being obtained of the azo-class and shown to possess dyeing powers. As Dr. Caro has referred to this in his notice in the *Berichte* of the late Peter Griess, I need not make any further observations on the subject here (*Ber.*, 1892, **25**, 4, 1011).

At this period much interest was taken in the artificial formation of natural organic substances; but at the time I was at the Royal College of Chemistry, although the theory of compound radicles, the doctrine of substitution, &c., were occupying much attention, very little was known of the internal structure of compounds and the conceptions as to the method by which one compound might be formed from another was necessarily very crude.

Thus, in the Report of the Royal College of Chemistry, published in 1849, Hofmann refers to the artificial formation of quinine as a great desideratum, and then states

"It is a remarkable fact that naphthalene, the beautiful hydrocarbon of which immense quantities are annually produced in the manufacture of coal gas, when subjected to a series of chemical processes, may be converted into a crystalline alkaloïd. This substance, which has received the name of naphthalidine, contains 20 equivalents of carbon, 9 equivalents of hydrogen, and 1 equivalent of nitrogen." (C = 6. O = 8.)

* * * * *

"Now if we take 20 equivalents of carbon, 11 equivalents of hydrogen, 1 equivalent of nitrogen, and 2 equivalents of oxygen, as the composition of quinine, it will be obvious that naphthalidine, differing only by the elements of two equivalents of water, might pass into the former alkaloid simply by an assumption of water. We cannot, of course, expect to induce the water to enter merely by placing it in contact, but a happy experiment may attain this end by the discovery of an appropriate metamorphic process."

In fact there was but little other ground to work upon in many instances than this kind of speculation.

As a young chemist I was ambitious enough to wish to work on this subject of the artificial formation of natural organic compounds. Probably from reading the above remarks on the importance of forming quinine, I began to think how it might be accomplished, and was led by the then popular additive and subtractive method to the idea that it might be formed from toluidine by first adding to its composition C_3H_4 by substituting allyl for hydrogen, thus forming allyltoluidine, and then removing two hydrogen atoms and adding 2 atoms of oxygen, thus

$$\underbrace{2(C_{10}H_{13}N)}_{\text{Allyltoluidine.}} + 3O = \underbrace{C_{20}H_{24}N_2O_2}_{\text{Quinine.}} + H_2O$$

The allyltoluidine having been prepared by the action of allyl iodide on toluidine, was converted into a salt and treated with potassium dichromate; no quinine was formed, but only a dirty reddish-brown precipitate. Unpromising though this result was, I was interested in the action, and thought it desirable to treat a more simple base in the same manner. Aniline was selected, and its sulphate was treated with potassium dichromate; in this instance a black precipitate was obtained, and, on examination, this precipitate was found to contain the colouring matter since so well known as *aniline purple* or *mauve*, and by a number of other names. All these experiments were made during the Easter vacation of 1856 in my rough laboratory at home. Very soon after the discovery of this colouring matter, I found that it had the properties of a dye, and that it resisted the action of light remarkably well.

After the vacation, experiments were continued in the evenings when I had returned from the Royal College of Chemistry, and combustions were made of the colouring matter. I showed it to my friend Church, with whom I had been working, on his visiting my laboratory, and who, from his artistic tastes, had a great interest in colouring matters, and he thought it might be valuable and encouraged me to continue to work upon it; but its evident costliness and the difficulties of preparing aniline on the large scale, made the probability of its proving of practical value appear very doubtful. Through a friend, I then got an introduction to Messrs. Pullar, of Perth, and sent them some specimens of dyed silk. On June 12, 1856, I received the following reply:—

"If your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a very long time. This colour is one which has been very much wanted in all classes of goods, and could not be obtained fast on silks, and only at great expense on cotton yarns. I enclose you pattern of the *best* lilac we have on cotton—it is dyed only by one house in the United Kingdom, but even this is not quite fast, and does not stand the tests that yours does, and fades by exposure to air. On silk the colour has always been fugitive: it is done with cudbear or archil, and then blued to shade."

This somewhat lengthy extract is quoted because it gives a glimpse at the state of the dyeing trade in reference to this shade of colour at that period.

This first report was very satisfactory; the "if" with which it commenced was, however, a doubtful point.

During the summer vacation, however, the preparation of the colouring matter on a very small, technical scale was undertaken, my brother (the late T. D. Perkin) assisting me in the operations, and, after preparing a few ounces of product, the results were thought sufficiently promising to make it desirable to patent the

process for the preparation of this colouring matter. This was done on August 26, 1856 (Patent No. 1984). A visit was then made to Messrs. Pullar's, and experiments on cotton dyeing were made, but, as no suitable mordants were known for this colouring matter, only the pale shades of colour, produced by the natural affinity of the dye for the vegetable fibre, were obtained; these, however, were admired. Experiments on calico printing were also made at some print works, but fears were entertained that it would be too dear, and, although it proved to be one of the most serviceable colours as regards fastness, yet the printers were not satisfied with it because it would not resist the action of chloride of lime like madder purple.

Although the results were not so encouraging as could be wished, I was persuaded of the importance of the colouring matter, and the result was that, in October, I sought an interview with my old master, Hofmann, and told him of the discovery of this dye, showing him patterns dyed with it, at the same time saying that as I was going to undertake its manufacture, I was sorry that I should have to leave the Royal College of Chemistry. At this he appeared much annoyed, and spoke in a very discouraging manner, making me feel that perhaps I might be taking a false step which might ruin my future prospects. I have sometimes thought that, appreciating the difficulties of producing such compounds as aniline and this colouring matter on the large scale, Hofmann perhaps anticipated that the undertaking would be a failure, and was sorry to think that I should be so foolish as to leave my scientific work for such an object, especially as I was then but a lad of 18 years of age; and I must confess that one of my great fears on entering into technical work was that it might prevent my continuing research work, but I determined that, as far as possible, this should not be the case.

Still, having faith in the results I had obtained, I left the College of Chemistry and continued my experiments, and found that not only aniline, but also toluidine, xylidine, and cumidine gave a purple colouring matter when oxidised.

The following is a copy of the principal part of the complete specification of the patent I took out at this time:—

"*Dyeing Fabrics.*

"The nature of my invention consists in producing a new colouring matter for dyeing with a lilac or purple colour stuffs or silk, cotton, wool, and other materials in the manner following:—

"I take a cold solution of sulphate of aniline, or a cold solution of sulphate of toluidine, or a cold solution of sulphate of xylidine, or a cold solution of sulphate of cumidine, or a mixture of any one of such solutions with any others or other of them, and as much of a cold solution of a soluble bichromate as contains base enough to convert the sulphuric acid in any of the above-mentioned solutions into

a neutral sulphate. I then mix the solutions and allow them to stand for 10 or 12 hours, when the mixture will consist of a black powder and a solution of a neutral sulphate. I then throw this mixture upon a fine filter, and wash it with water till free from the neutral sulphate. I then dry the substance thus obtained at a temperature of 100° C., or 212° F., and digest it repeatedly with coal-tar naphtha, until it is free from a brown substance which is extracted by the naphtha. Any other substance than coal-tar naphtha may be used in which the brown substance is soluble and the colouring matter is not soluble. I then free the residue from the naphtha by evaporation, and digest it with methylated spirit, or any other liquid in which the colouring matter is soluble, which dissolves out the new colouring matter. I then separate the methylated spirit from the colouring matter by distillation, at a temperature of 100° C. or 212° F."

Fresh quantities of colouring matter were prepared and taken to Scotland, and, although the method of applying it by means of lacterine (casein) was then found to give very good results, yet the printers who tried it did not show any great enthusiasm; and even Messrs. Pullar began to fluctuate in their opinion as to the advisability of erecting plant for its manufacture, and wrote:—"Should it appear that it will not be of service to printers, it will be questionable whether it would be wise to erect works for the quantity dyers alone will require." In January, 1867, Mr. R. Pullar, however, advised me to see Mr. Thos. Keith, a silk dyer of Bethnal Green, London, and, after making a few experiments with the colouring matter, and exposing the specimens he dyed to the light for some time, he was much pleased with the result, and encouraged me to go on with its production.

I was then joined in the undertaking by my father—who was a builder, and had sufficient faith in the project to risk the necessary capital—and also by my brother, who also had a good knowledge of building, and, as he had taken part in the preliminary experiments on the preparation of the dye, his assistance proved most valuable, especially as he was possessed of good business capabilities. Plans were prepared and a site obtained at Greenford Green, near Harrow, and in June, 1857, the building of the works was commenced.

At this time, neither I nor my friends had seen the inside of a chemical works, and whatever knowledge I had was obtained from books. This, however, was not so serious a drawback as at first it might appear to be, as the kind of apparatus required and the character of the operations to be performed were so entirely different from any in use that there was but little to copy from.

In commencing this manufacture, it was absolutely necessary to proceed tentatively, as most of the operations required new kinds of apparatus to be devised and tried before more could be ordered to carry out the work on any scale.

But the mechanical were not the only difficulties. Benzene at this

time was only made to a very limited extent, as there was but little use for it, and it was only after making several inquiries that it was ascertained where it could be obtained. That used at first came from Messrs. Miller and Co., of Glasgow. It was also of very unequal quality, and required refractionating before use; its price was 5*s*. per gallon. No nitric acid sufficiently strong for the preparation of nitrobenzene could be obtained commercially, and, as we did not want to complicate our works by manufacturing the substance, experiments were made with a mixture of sodium nitrate and sulphuric acid, using the latter in rather larger proportions than necessary to give an acid sodium sulphate. This method was found to succeed on the small scale, but, when working with large quantities, special apparatus had to be devised, and a great many precautions had to be taken to regulate the operation; however, very large quantities of nitrobenzene were made by it. Nitrobenzene had never been prepared in iron vessels before this time.

It was only three years before the works were started that Bechamp had made the interesting discovery that finely divided iron and acetic acid were capable of converting nitrobenzene into aniline; had it not been for this discovery, the coal-tar colour industry could not have been started. To carry this process out on the large scale, special apparatus was also required, and, on account of the energy of the action which takes place, special precautions had to be adopted; but no great difficulties were encountered in this operation. Potassium bichromate at that date fluctuated between $9\frac{3}{4}d.$ and 11*d*. per lb., and was therefore a costly product.

Many more details might be gone into in reference to the difficulties to be contended against at the starting of the industry, but sufficient has been said to give some idea of them; however, in less than six months after the building of the works was commenced, namely, in December, 1857, aniline purple, or Tyrian purple, as it at first was called, was in use for silk dyeing in Mr. Keith's dye-house.

But in dyeing large quantities of silk, difficulties were again encountered, on account of the great affinity of the colouring matter for the fibre causing unevenness, and some time was taken up in experimenting on this subject, until eventually it was found that by dyeing in a soap bath a very pure and even colour could be produced. This process was afterwards found to be the most suitable for dyeing silk with magenta, Hofmann's violet, and many other colouring matters.

Aniline purple having now been proved to be an important colouring matter, which could be produced on a manufacturing scale, it attracted much attention, and, as a consequence, many others com-

menced its manufacture, and also to experiment with aniline, especially in France; all kinds of oxidising agents were used, but potassium dichromate still proved to be the best, the next best being chloride of copper, the use of which was patented by Dale and Caro, in 1860.

The French manufacturers were not long before they succeeded in producing the colouring matter (the French patent being invalid, owing to a mistake as to the date it was necessary to take it out in reference to that of the English patent), and in using it in dyeing their goods, both silk and cotton. The calico printers of this country then began to be alive to the necessity of following them, and this made the demand for the aniline purple—which the French now began to call mauve—so great that, notwithstanding the continued increase which had been taking place in the works at Greenford Green, it could not be kept pace with. At this time, a very beautiful archil colour had been produced by Messrs. Guinon, Marnas, and Bonney, called French purple; this also was applied to calico printing, and the printers in this country who could not get a supply of aniline purple used this until their requirements could be met. A little before this, Mr. Pullar and I separately discovered a process for mordanting cotton, so that it could be dyed with aniline purple to any depth of colour, and thus it became of much more value to the cotton dyer than it was so long as its natural affinity for the fibre could alone be relied upon. The process consisted in the use of tannin and a metallic oxide.

For calico printing, the colouring matter was first applied in combination with lacterin, albumin, or gluten, but endeavours were soon made to find some new method by which these might be dispensed with, and I worked for some considerable time on this subject at the Dalmonach Print Works, Alexandria, Dumbartonshire, where the colour was first practically used for printing in this country. I devised a process, which consisted in printing on a lead salt, converting this into a salt containing a fatty acid by means of soap, and then dyeing in a soap bath containing the colouring matter; the fatty lead salt then took up the colouring matter, whilst the soap prevented the white from being stained; this process was patented by myself and Mr. Mathew Grey. It produced beautiful shades of colour, but could not be used where combinations with other colours were required, and therefore did not prove useful.

Printers then experimented on the use of tannin and a metallic oxide, the process used in cotton dyeing devised by Mr. Pullar and myself; a modified form of this process has become the most important used. Another process was also very largely used, patented by M. Schultz and myself, which consisted in forming an

insoluble arsenite of alumina and colouring matter on the fibre, the colours produced in this way being very brilliant, as well as fast to washing. Before the aniline purple could be introduced for dyeing woollen and mixed fabrics, some weeks were also spent at Bradford in finding out suitable methods of applying it.

Thus it will be seen that, in the case of this new colouring matter, not only had the difficulties incident to its manufacture to be grappled with, and the prejudices of the consumer overcome, but, owing to the fact that it belonged to a new class of dye stuffs, a large amount of time had to be devoted to the study of its applications to dyeing, calico printing, &c. It was, in fact, all pioneering work—clearing the road, as it were, for the introduction of all the colouring matters which followed, all the processes worked out for dyeing silk, cotton, and wool, and also for calico printing, afterwards proving suitable for magenta, Hofmann violet, &c.

All this time a host of experimentalists continued making trials with aniline and all kinds of chemicals, and early in 1859, three years after the discovery of aniline purple, or mauve, M. Verquin discovered fuchsine, also called magenta and roseine, and, later on, rosaniline by Hofmann.

From what has been said above, it will be seen that the discovery of this colouring matter was made under more favourable auspices than that of mauve: everything was ready for its production and application, it was also an easier product to manufacture and relatively to the aniline used was formed in much larger quantities than mauve was, but it was not nearly so fast against light, and when first experimented with I thought this would have been very detrimental to its extensive use, remembering the experience that I had gone through with mauve; but things had changed, and the love of brilliancy had begun to outrun the regard for durability, indeed, as is well known, magenta has proved to be one of the most successful of the coal-tar colours ever discovered. M. Verquin's process was a very remarkable one, and it has never transpired whether he was led to it by any scientific reasoning or not; it will be remembered that it consists in heating commercial aniline and anhydrous tetrachloride of tin nearly up to the boiling point of the mixture; it was first carried out by Messrs. Reynard Bros., of Lyons.

We were thus indebted to France for the second step in the coal-tar colour industry. Soon other processes were invented for the production of magenta, but the most practical one, after M. Verquin's, was that in which mercury nitrate was used; large quantities of colouring matter were made by this method.

The fuchsine, or magenta, first made in France, was but very imperfectly purified, and a good deal of that afterwards made in

Germany simply consisted of the "melt" produced by heating aniline with mercury nitrate.

Being naturally interested in this new colouring matter, I made many experiments with it. and in a lecture I delivered before this Society, on May 16, 1861 (*J. Chem. Soc.*, 1862, **14**, 230) (when I was honoured by the presence of Michael Faraday), an account of some of the results obtained by its examination was given, in which it was shown that it was the salt of an organic base (a fact at that time believed in by some, but doubted by others) precipitated by alkalis and at the same time dissolved by them to some extent, yielding colourless solutions, and that its nitrate could be obtained in the form of octahedrons, having a beautiful green metallic reflection; this was the first occasion, I believe, on which it was described as a crystalline compound. Attention was also called to the fact that its salts could not contain oxygen, which was afterwards confirmed by Hofmann; and it was further pointed out that other products were formed along with it, one possessing an orange colour (chrysaniline), and another a purple colour (violaniline, mauve aniline, &c.).

In speaking of the manufacture of rosaniline in this country, I must first refer to another of Hofmann's pupils, Edward Chambers Nicholson, of the firm of Simpson, Maule and Nicholson, who brought the manufacture of this compound to a state of perfection, which, I believe, has not been surpassed—so far as purity is concerned—up to the present time.

It is of interest to trace the manner in which Messrs. Simpson, Maule and Nicholson, became connected with the coal-tar colour industry. They were originally manufacturers of fine chemicals, &c. When aniline purple was found to be successful, and was exciting a great deal of interest, this and other firms were anxious to manufacture it, and consequently wished to have a licence for the purpose, but no agreement could be come to. They were then very desirous of manufacturing nitrobenzene for our use in producing aniline. At first they could not do this at a sufficiently low price, but eventually succeeded in producing it cheaply enough to make it worth our while to supplement our own make by theirs, as the demand for aniline purple was then so rapidly increasing. In this way they soon became considerable producers of nitrobenzene; they then set to work to prepare aniline, which after a time they succeeded in doing. In this manner they leisurely, as it were, became fully prepared to go a step further, and become manufacturers of colouring matters.

Dr. David Price at this time joined the firm, and Nicholson and he apparently experimented with the products he had patented in 1859, namely violin, purpurin, and roseine, obtained by oxidising aniline with lead peroxide; these colouring matters, however, were not found

to be of practical value. They then turned their attention to the newly discovered colouring matter, fuchsine. This they commenced manufacturing, giving it the name of one of Dr. Price's products "roseine."

H. Medlock, another of Hofmann's pupils at the Royal College ot Chemistry, took out a patent on January 18, 1860, for the production of magenta, by heating aniline with arsenic acid; eight days later, Nicholson filed a similar patent, but did not proceed with it when he learnt what Medlock had done. Medlock's patent is notorious for the amount of litigation that arose owing to the occurrence in it of the word "anhydrous." The formation of magenta by the use of arsenic acid proved in the hands of Nicholson, and also of others, a great improvement on the previous processes, and for a long time was *the* process for the production of this colouring matter, until, in fact, it was superseded by the use of nitrobenzene instead of arsenic acid.

One of the things Hofmann used to impress on those of his students who were engaged at research work was the great importance of preparing their products in as nearly pure a condition as possible—especially those which were to be submitted to analysis; some of us used to think that we should get as good results by examining the substances when crystallised fewer times than he required, especially when the products were difficult to obtain and the quantities became smaller and smaller on each recrystallisation; but he was right. Nicholson, when at the Royal College, made several investigations under Hofmann's direction, studying the compounds of phosphoric acid with aniline; the formation of cumidine from cumene from cuminic acid; also caffeïne and some of its compounds; and, in conjunction with F. A. Abel, he investigated strychnine. He also appears to have been an adept at combustions, as he made the combustion of benzene for Mansfield; his name appearing also in de la Rue's paper on cochineal as having made one of the combustions of nitrococcusic acid. There is no doubt that Hofmann's teaching as to the importance of working with pure materials was strongly impressed upon Nicholson when carrying on these researches, and that it greatly influenced him when he became engaged in the manufacture of colouring matters. It is only right to add that Dr. D. Price, with whom he was for some time associated in this industry, and whom I knew when at the Royal College of Chemistry as a most thorough, painstaking, and careful worker, would also second his efforts in this respect. I may also add that I feel sure Hofmann's influence in this direction had also a considerable influence on my own after career as a chemist.

At first Messrs. Simpson, Maule, and Nicholson supplied magenta, or

roseine, as they called it, to the dyers in alcoholic solution, but afterwards, when they had obtained it in a pure condition, they sold it in crystals (usually the oxalate). In their process of purification they boiled the crude solution of the colouring matter with milk of lime, and collected the base which deposited from the clear solution thus obtained, and from this prepared the desired salts.

By this time the coal-tar colour industry had become one of no mean dimensions in this country, and also in France, and it was quickly developing in Germany and elsewhere. The number of colours was also increasing, for not only had mauve or aniline purple and fuchsine been discovered, but Gerard and Delaire had made their remarkable discovery of *Imperial violet* and *Blue de Lyon* by heating aniline with fuchsine, thereby—as is now known—*phenylating* this colouring matter.

When first speaking of fuchsine, I mentioned that it was discovered by M. Verquin, and, from a practical point of view, this may be considered correct. Nevertheless it appears to have been first seen as far back as 1856, when Natanson (*Annalen der Chemie und Pharmacie*, 1856, **98**, 297) observed that in heating aniline and chloride of ethylene in a sealed tube to 200°, the mixture becomes of a rich blood-red colour; Hofmann also, in 1858, when acting on aniline with carbon tetrachloride obtained, besides carbotriphenyltriamine, a small quantity of this substance as a secondary product, which he describes as "a very soluble substance of a magnificent crimson colour." *

In the Report of the Exhibition of 1862 (Class II, sec. A, p. 126), Hofmann, in speaking of the discovery of this colouring matter, says:—"It may be said to have been discovered at two different times according as the question is considered from a scientific or industrial point of view;" and at p. 126:—"Industrially, the discovery of aniline red was made by Messrs. Verquin and Renard Brothers of Lyons."

The investigation Hofmann made with the Nicholson products soon set at rest the conflicting views which at first existed in reference to this colouring matter, and proved that it was a well defined triamine —which he re-named *rosaniline*—forming salts free from oxygen. He then regarded the base, which had the formula $C_{20}H_{21}N_3O$, as a

* About two years after M. Verquin's discovery of fuchsine, the use of carbon tetrachloride and aniline as a means of preparing this colouring matter was tried, for reasons connected with patent rights, by MM. Monnet and Drury of Lyons. They first employed a temperature of 116—118° until the reaction between these two substances was over, and then heated the product up to 170° or 180°. By this means of working, they apparently obtained a larger yield than Hofmann, but the process never became a practical one. See *Moniteur Scientifique*, T. III, 15 Jan., 1861.

hydrate of the anhydrous compound $C_{20}H_{19}N_3$. Hofmann examined many of the salts of rosaniline—those with one molecule of acid, the ordinary salts used in dyeing, and the hydrochloride with 3 mols. of acid. He also obtained the interesting compound, leucaniline, by treating rosaniline with reducing agents, a compound which has its representation in all triphenylmethane colouring matters. The investigation is a memorable one, as being the first investigation which gave correct information respecting the formula of a coal-tar colouring matter.

It had been observed by manufacturers that some varieties of aniline yield much more rosaniline than others, samples boiling at temperatures much higher than the boiling point of the pure compound being found particularly adapted for the production of the red; and it appears that Nicholson had ascertained that pure aniline was incapable of yielding rosaniline. Hofmann studied this subject, using aniline prepared from indigo and from pure benzene, and his experiments confirmed Nicholson's. The idea then naturally suggested itself, that the toluidine contained in commercial aniline might be the source of the colouring matter. But, on making experiments with toluidine (orthotoluidine was not then known) it was found that this base also was incapable of producing the dyestuff; on taking a mixture of aniline and toluidine, however, it was at once produced in quantity, showing that both bases were necessary for its production (Report, International Exhibition, 1862, Class II, sec. A, 130).

This discovery was of great importance and interest, and explained most of the facts connected with the use of anilines of different boiling points. In the case of mauveïne, this discovery was not of so great importance as in the case of rosaniline, because pure aniline yields a purple colouring matter (pseudomauveïne), as well as mixtures of aniline and toluidine.

Mauve had also been obtained in a pure crystallised condition, but technically this was not found of much advantage, as the colours obtained with it in this condition were only slightly superior to those obtained with the less expensive precipitated colouring matter which was usually supplied to the consumer.

Having examined aniline red or rosaniline, Hofmann was also desirous of investigating aniline purple or mauve, but when he spoke to me on the subject, the colouring matter was already under investigation in my own laboratory.

The crystallised aniline purple sent into the market was the acetate of the base to which I gave the name mauveïne. This base is remarkable for its stability and tinctorial power. Its investigation (1864, *Proc. Roy. Soc.*, **12**, 713) showed that it possesses the formula $C_{27}H_{24}N_4$, and

that, unlike rosaniline, it is not a hydroxy-compound. Moreover, the base is a strongly coloured compound of a blue-violet colour. When treated with reducing agents, it yields a leuco-compound, but this is so sensitive to the action of oxygen that on exposure to the air it instantly changes back to mauveïne. Its ordinary salts are produced from 1 mol. of base and 1 mol. of acid. From a more recent research on this colouring matter (*J. Chem. Soc.*, 1879, 717), I have shown that a dihydrochloride and corresponding platinum salt can be obtained, and from the characteristic changes which a solution of this substance, in concentrated sulphuric acid, undergoes on dilution, namely, from a dull green to a blue, and lastly to a purple, shows that probably salts formed by the union of mauveïne with more than 2 mols. of acid exist. The ordinary commercial product has also been shown to consist of two colouring matters, one forming very soluble and apparently uncrystallisable salts called pseudomauveïne, having the formula $C_{24}H_{20}N_4$, and produced from pure aniline; the other forming less soluble and beautifully crystalline salts of the formula $C_{27}H_{24}N_4$, derived from paratoluidine and aniline. This colouring matter, unlike rosaniline, does not freely undergo changes with reagents on account of its great stability, so that few derivatives have been obtained from it serving to elucidate its constitution, which is still unknown.

Messrs. Simpson, Maule, and Nicholson, after engaging in the manufacture of rosaniline for some time, undertook that of Girard and Delaire's Imperial Violet and Blue de Lyon, obtained by heating a salt of rosaniline with aniline (Pat., January, 1861).

Mr. Nicholson spent much time in studying the conditions most favourable to the production of these compounds, especially the blue, so as to obtain it in a pure condition, and in this he was very successful. This was due to his knowledge of the importance of using pure materials in its manufacture. The rosaniline base he used was not merely the best he produced for the preparation of rosaniline salts, but he purified it much further by means of methylated spirit; the aniline was prepared for the purpose from the purest benzene he could obtain; he also paid much attention to the selection of the best acid to use in combination with rosaniline, and found that weak organic acids, such as acetic and benzoic acids, were the most suitable. In this way he eventually obtained the blue in a condition of purification unequalled by others.

Provided with the purified blue by Nicholson, Hofmann soon discovered that the base had the formula $C_{38}H_{33}N_3O$; this he regarded as a hydrate of the compound $C_{38}H_{31}N_3$, of which he obtained a hydrochloride of the composition $C_{38}H_{31}N_3HCl$. The blue was converted by reducing agents into a leuco-compound.

As far back as 1850 (*Phil. Trans.*, **1**, 93, *J. Chem. Soc.*, **3**, 283), when engaged in his researches on the molecular constitution of the volatile organic bases, Hofmann had endeavoured to displace the hydrogen in aniline by phenyl, by heating it with phenol, but was unsuccessful; we can, therefore, easily understand his delight when he found that on boiling rosaniline with aniline the colouring matter became phenylated. The long desired method of effecting the displacement of hydrogen by phenyl had, in fact, been discovered, and we find that no sooner had he recognised that the blue was a triphenyl rosaniline than he telegraphed the result to Paris.* The *Comptes rendus* of the sitting of the Academy of May 18th, 1863, contains the following note:

"M. Le Secrétaire Perpétuel communique une Courte Note de M. Hofmann conçue dans les terms suivants.

"Bleu d'Aniline.—En poursuivante mes recherches sur les couleurs d'aniline, je suis arrivé à un résultat très simple; le bleu d'aniline est la rosaniline triphényliqne: une molécule de rosaniline et trois molécules d'aniline renferment les éléments d'une molécule de bleu d'aniline et trois molécules d'ammoniaque."

The paper, communicating fuller details of his results on this colouring matter, was read on July 6th of the same year (*Compt. rend.*, 1863, **57**, 25). Speaking in this paper of Nicholson, he pays him this tribute: "That in him was united the genius of the manufacturer and the habits of a scientific investigator."

We find the discovery of the phenylation of rosaniline afterwards bearing fresh fruit in the hands of Delaire, Gerard, and Chapoteaut, who established the remarkable fact that when boiled with its own hydrochloride, aniline acted in a similar manner, producing diphenylamine and ammonia; by using aniline hydrochloride and toluidine, they, in like manner, obtained phenyltoluylamine (*Compt. rend.*, 1866, **63**, 91).

Aniline blue having proved to be triphenylrosaniline, it was soon seen that the different shades of violet imperial were rosanilines more or less phenylated.

Nicholson also found that, on heating acetate of rosaniline to 200—215°, ammonia was disengaged, and a purple colouring matter produced, which he called regina purple. This substance was found to be a monophenylrosaniline (patented January 20, 1862).

One of the great obstacles in the way of the application of aniline

* Hofmann had made this discovery apparently on the same day, for Professor McLeod who was his assistant at that time, gives me an entry from his diary dated May 18th, 1863, which runs thus: "The doctor told me that he had made a fine discovery, and that aniline blue is the triphenylated rosaniline. Rosaniline, $C_{20}H_{19}N_3H_2O$; aniline blue, $C_{20}H_{16}(C_6H_5)_3N_3H_2O$."

blue was its slight solubility in water, which rendered the dyeing operations unsatisfactory; this also militated against its use in calico printing for some time (the most suitable process for its use for this purpose first found being that of Schultz and myself with arsenate of alumina, but with this long steaming and afterwards clearing in a soap bath was required; the colours thus obtained, however, were very pure and very durable). Nicholson naturally was very desirous of overcoming this obstacle, and no doubt the well known process of rendering indigo soluble by dissolving it in sulphuric acid, and then converting it into a sulphonic acid, occurred to him; at any rate, by experimenting in this direction, he succeeded in obtaining the desired result and patented the process (June 1, 1862). Nicholson obtained two sulphonic acids—a mono- and a tri—the first being known as Nicholson's blue, and the latter as soluble blue, and it is owing to the discovery of these derivatives of aniline blue or triphenylrosaniline that this colouring matter became of such importance.

This method of treating aniline blue was very interesting as being the first instance of sulphonating an aniline colour, a process which of late years has become of so much importance, not only in rendering difficultly soluble dyes soluble, but also in changing the chemical nature of the colouring matters, and thus extending their applications as dyes, as in the case of rosanilinesulphonic acid.

It was Nicholson who succeeded in isolating the yellow or orange colouring matter which is formed in the manufacture of rosaniline; he prepared it in a pure state, and called it "phosphine." Hofmann undertook the examination of this dye, and showed that it is represented by the formula $C_{20}H_{17}N_3$, differing from that of rosaniline in containing 2 atoms of hydrogen less; the base is capable of forming salts with 1 or 2 mols. of hydrochloric acid, the nitrate being remarkable for its insolubility.

After discovering that aniline blue or bleu de Lyon was a triphenylrosaniline, Hofmann was very naturally inclined to experiment on rosaniline with the agents he had used so successfully in his experiments on the molecular constitution of the volatile organic bases, namely, the haloïd compounds of the alcohol radicles, to see what influence these radicles would have if introduced into the base: he found that they had, like phenyl, though not to the same extent, a blueing effect, the colour changing from red to purple, and then to violet as the hydrogen atoms were gradually displaced, colouring matters being produced which were found to be of great beauty when applied to silk, &c. In his first paper on these products (*Compt. rend.*, 1863, **57**, 30), he gives an account of the action of methyl, ethyl, and amyl iodides on rosaniline, and amongst the products he obtained at that time describes the highest ethylated derivative he

had succeeded in producing as the iodethylate of triethylrosaniline, $C_{20}H_{16}(C_2H_5)_3N_2{\cdot}C_2H_5I$.

He patented the method of producing these colouring matters on May 22, 1863.

It is easy to see how Hofmann was led to the production of these compounds in the regular sequence of his work, but it is curious that E. Kopp had evidently prepared some of them as long back as 1861. E. Kopp remarks in his paper in the *Comptes rendus*, 1861, **52**, 363, "I have only stated in my notice these substitutions as a hypothesis, but their existence is very real; I have already obtained some of them, and it is a remarkable thing that the red shade disappears, and is converted into a violet, becoming bluer and bluer as the hydrogen is displaced by the hydrocarbons." It appears that he sent some specimens of his products to M. Dumas.

When Hofmann patented the use of methyl, ethyl, and amyl iodides for the preparation of these colouring matters, it seemed almost incredible that substances such as these, which had hitherto only been used in research, should be employed in the manufacture of a dye; but such circumstances have constantly arisen in the history of this remarkable industry—aniline itself, the parent of artificial colours, being an example—and nothing now appears to be too rare or difficult to prepare, to be used in its development.

It is difficult to understand why E. Kopp did not go on with his work on these substitution compounds, unless it was owing to the fact that rosaniline was expensive in his days, and he considered the alcoholic haloïds too costly to employ for practical purposes.

The Hofmann violets were the most brilliant in colour of any which had been produced, and proved not to be so costly as might be anticipated, as the iodine from the ethyl iodide used could be mostly recovered; but these colouring matters have not the stability of mauve or imperial violet, and at first it was thought that their use would be limited, but the increasing desire for brilliancy was still superseding that for stability, and the result was, that these colouring matters were very largely used, and interfered very considerably with the sale of the mauve and imperial violets, except for pale shades of colour, when, unless the colouring matter used be stable, the goods fade so quickly as to be of little value.

The products formed on heating mauveïne salts with aniline apparently are not comparable with those obtained from rosaniline, and although the product becomes bluer no ammonia is evolved; from my later experiments, it seems most likely that the aniline used takes no part in the change, the blueing being a change in the colouring matter, the consequence of the temperature employed.

When treated with ethyl iodide, mauveïne behaves unlike rosanil-

ine, yielding a beautiful colouring matter, which is of a *redder* shade, and not bluer as in the latter case. This colouring matter, called *dahlia* (patented on November 6, 1863), consists of a monethylic derivative of mauveïne, its hydrochloride being represented by the formula, $C_{27}H_{23}(C_2H_5)N_4,HCl$. No further change is effected by ethyl iodide, and it is uncertain whether the product is a substitution or an addition compound (it may be remarked here that at times some quantity of a dark, blue-black, almost insoluble substance containing iodine is also produced).

This dahlia or ethylmauveïne was used by the calico printers and dyers to some extent, though not largely, on account of its costliness. It is, however, a colouring matter, which gives shades of very considerable stability on exposure to light.

The discovery that the introduction of such radicles as phenyl or ethyl altered the colour of rosaniline so greatly, made it of interest to see whether other kinds of hydrocarbon groups could be introduced to modify its tint. Amongst other products, brominated turpentine was used, and on heating it with rosaniline hydrochloride dissolved in methylated spirit or methyl alcohol under pressure, it was found that a very beautiful purple or violet colouring matter could be produced; the process was patented in 1864, and large quantities of a colouring matter, known as *Britannia violet*, were prepared in this manner. At first it was thought that the hydrocarbon radicle of the brominated turpentine entered the rosaniline, but it now appears most probable that the product consisted of methylrosanilines produced by the action of methyl bromide formed from hydrogen bromide resulting from the decomposition of the bromo-compound. The colouring matter was more soluble than Hofmann's ethyl violet, but I could not succeed in crystallising it, and, therefore, it was not subjected to analysis.

When the base of Britannia violet is acted on by acetyl chloride, two products are obtained, namely, a violet colouring matter much bluer in shade than the original violet, and a bluish-green compound. The base of this latter has a very feeble affinity for acids, and does not combine with acetic acid, whilst the base of the violet compound does so freely, and in virtue of these different properties the two colouring matters are easily separated. The green dye proved to be of practical value, and considerable quantities of it were prepared for the calico printers, and was known as "Perkins green;" but after a time it was displaced by iodine green. It has not hitherto been investigated. For its manufacture, large quantities of terchloride of phosphorus were prepared, from which and acetic acid large quantities of acetyl chloride were made—another instance of the use of a research reagent on the large scale.

The last investigation relating to colouring matters carried out by Hofmann in this country was that of the very interesting substance known as *chinoline blue*, discovered by Greville Williams, of which the latter gave an account in the *Chemical News* for October 11, 1860 (p. 219). A beautiful specimen of the crystallised substance was displayed in the exhibition of 1862 under the name of *Cyanin*. Chinoline blue was of a very pure shade of colour, and, although an expensive product, attempts were made to introduce it as a dye; unfortunately, although produced from bases of remarkable stability, it was very fugitive, goods dyed with it fading very quickly indeed when exposed to the light—its sensitiveness being so great that on placing it under a glass positive photograph and exposing to sunlight, after only a short time, a chinoline blue positive picture was produced.

Hofmann separated from chinoline two blue compounds, to one of which he gave the formula $C_{30}H_{39}N_2I$, and to the other the formula $C_{28}H_{35}N_2I$. According to later researches, the blue is a condensation product derived from chinoline amyliodide and lepidine amyliodide.

$$\underset{\text{Chinoline amyl iodide.}}{C_9H_7N\cdot C_5H_{11}I} + \underset{\text{Lepidine amyl iodide.}}{C_{10}H_9N\cdot C_5H_{11}I} + O = \underset{\text{Cyanine or diamyl cyanine iodide.}}{C_{29}H_{35}N_2I} + H_2O + HI$$

This formula differs from that given by Hofmann to one of the products he examined by an atom of carbon only.

After I left the Royal College of Chemistry, the researches on the phosphorus bases in which I had been helping were continued by Drs. Leibius and Holzmann, to whose able assistance Hofmann refers in one of his papers; but in carrying out the part of this work relating to the phosphammonium, phospharsonium, and arsammonium compounds, another assistant was active who is referred to by Hofmann in the following words:—

"I conclude this mémoir with the expression of my best thanks for the untiring patience with which Mr. Peter Griess has assisted me in the performance of my experiments on the phosphorus bases. The truly philosophical spirit in which this talented chemist has accompanied me through the varying fortunes of this inquiry, will always be one of my pleasing recollections."

We know how the high opinion thus expressed by Hofmann of Griess not only lasted, but became enhanced as time went on; and although Griess was not one of Hofmann's pupils, I cannot refrain from thus referring to him here, as several of his most important early researches on the diazo-compounds were made within the walls of the Royal College of Chemistry, thereby connecting this Institution with work which of late years has had such a marvellous

influence on the development of the coal-tar colour industry. But it is not my intention, nor indeed is it necessary for me, to go into the history of the diazo-compounds, as this has been so very ably done by my friend Caro in his memoir of Peter Griess, whom he held in such high esteem, and who was also one of his greatest friends.

Hofmann's departure was not only a cause of regret to those who had worked under him and to all his friends; it was a heavy loss also to the country at large, as no one had ever done so much for the cause of chemical science in the kingdom as Hofmann did, nor had any one exercised to such an extent that wonderful power he possessed of stimulating the enthusiasm of his students and of inciting in them a love of chemistry and of scientific research. His success is especially striking when the early history of the Royal College of Chemistry is taken into account—especially its financial difficulties, the dissatisfaction of some of the subscribers, and the want of understanding as to the value of scientific research shown both by them and the public at large. When all these circumstances are considered, we cannot but marvel at the courage and indomitable determination he displayed, which enabled him to overcome all difficulties and to persevere in maintaining the high standard of teaching he adopted at the beginning, as well as to continue the prosecution of scientific research for its own sake.

Notwithstanding the immense amount of work Hofmann must have had to attend to in connection with the building and fitting up of the new chemical laboratories of the Frederick William University of Berlin, which took place during the first four years after he left England, namely, from May, 1865, to May, 1869, no break occurred in his scientific activity, each year producing accounts of fresh work accomplished. It was not, however, until 1869 that he published anything fresh in connection with the coal-tar colours, but in this year several communications appeared.

Having found that the production of rosaniline depended on the presence of two bases, aniline and toluidine, he naturally carried his investigation of the subject further, and experimented with xylidine (meta). However, on heating this base with oxidising agents, either alone or in presence of toluidine, no colouring matter was obtained; but when it was heated with pure aniline, a red was formed, which he called xylidine red, which was supposed to be a homologue of rosaniline, probably of the composition $C_{22}H_{25}N_3O$. The colour produced on wool and silk by this dye-stuff was almost as bright as that of rosaniline itself (*Ber.*, **2**, 377). In a second paper relating to this subject, published in conjunction with Martius (*Ber.*, **2**, 411), an account

is given of similar experiments with an isomer of xylidine, amidoethylbenzene, which, from the more recent researches of Beilstein and Kuhlberg (*Zeitsch. f. Chem.*, [2], **5**, 524), we now know must have been a mixture of the ortho- and para-compounds. No red colouring matter was formed from this on boiling it with an oxidising agent, either alone or mixed with toluidine or even with aniline, thus affording proof of the interesting fact that an ethyl group cannot take the place of a methyl group in the interaction which is involved in the production of colouring matters of the rosaniline class.

After the discovery of mauve and magenta, many experiments were made with α-naphthylamine, as a source of colouring matter, and a variety of products were obtained and patented; but it is unnecessary for me to enter into an account of these here, as most of them were found to be of no technical value. I may, however, allude to two naphthalene derivatives which have proved useful; the first of these, naphthazarin, was discovered by Roussin in 1861, who thought it was artificial alizarin; this beautiful substance, which is now known to be a dihydroxy-β-naphthaquinone, lay dormant for a long time, but, owing to the discovery of improved methods of producing it, has of late come into use for dyeing black on wool. The second was discovered by Martius, and is known as "Martius yellow" or dinitro-α-naphthol. These were the principal colouring matters derived from naphthalene known prior to 1867, when Schiendl discovered the naphthalene red now known by the name of Magdala red, a substance remarkable for the beautiful fluorescence of its solution. The original process for its preparation consisted in heating naphthylamine, acetic acid, and potassium nitrite together, and then adding more naphthylamine and again heating until the desired colouring matter was produced.

Hofmann investigated this red, and assigned to it the formula $C_{30}H_{21}N_3$ (*Ber.*, 1869, **2**, 374).

As this colouring matter and the above formula appeared to be related to an old friend of mine, azodinaphthyldiamine (amidoazonaphthalene), I made it the subject of experiments, and found that it was easily produced on heating amidoazonaphthylene with an acid and naphthylamine, an action taking place which it was thought involved the displacement of an atom of hydrogen by naphthyl and the formation of ammonia:

$$\underset{\text{Azoamido-naphthaline.}}{C_{20}H_{15}N_3} + C_{10}H_9N = \underset{\text{Magdala red.}}{C_{30}H_{21}N_3} + NH_3$$

The colouring matter was called azotrinaphthyldiamine (*Proc. Roy. Inst.*, 1869, May 14).

In a second paper, published in July of the same year, on the nature of naphthalene red, Hofmann confirms my observation (*Ber*., **2**, 413).

It has since been shown, however, by Julius (*Ber*., 1886, **19**, 1365), that the action which occurs when amidoazonaphthalene is treated with naphthylamine is not nearly so simple as above indicated, and that the formula of the hydrochloride of Magdala red is $C_{30}H_{21}N_4Cl$, not $C_{30}H_{22}N_3Cl$.

The research on Magdala red led Hofmann to study the compound produced by the action of aniline on amidoazobenzene, a substance described by Martius and Griess, but discovered by Dale and Caro in 1863, and called by them *induline*. The examination of this product was afterwards continued by Hofmann in conjunction with Geyger, under the heading of colouring matters obtained from aromatic azodiamines, and published in 1872 (*Ber*., **5**, 472). They called this substance azodiphenyl blue, and showed that its hydrochloride had the formula $C_{18}H_{16}N_3Cl$.

In 1869 Hofmann also continued his researches on chrysaniline, studying the action of methyl and ethyl iodide on the base; he obtained trimethyl and triethyl substitution products (*Ber*., **2**, 378).

In preparing Hofmann violet, it was found that on precipitating the colouring matter from its aqueous solution by means of sodium chloride, a certain quantity of a bluish-green product remained in solution which could not be separated (though improved in colour) by the addition of sodium carbonate; this was precipitated by means of picric acid, and as it proved to be a valuable green dye, it, after a time, was supplied in small quantities to dyers under the name of iodine green. It was then found by J. Keisser (French patent, April 18, 1866) that the colouring matter could be obtained in much larger quantities by methylating rosaniline, dissolved in methyl alcohol, with methyl iodide, the operation being completed at a comparatively low temperature, and eventually it was obtained in a pure crystallised state. This substance being evidently related to the methylrosanilines, Hofmann was naturally interested in it, and with Girard undertook its investigation (*Ber*., **2**, 440).

The results they obtained, on analysing the iodo-compound, led them to represent it by the formula $\left.\begin{matrix}C_{20}H_{16}\\(CH_3)_3\end{matrix}\right\}N_3\left\{\begin{matrix}CH_3I\\CH_3\cdot I\cdot H_2O.\end{matrix}\right.$

They found that this compound decomposes when heated at the temperature of boiling water for a few hours, and instantly at 130—150°, becoming changed into a violet colouring matter; in fact, it behaves like an ammonium or addition product. As the complicated history of the methyl and ethyl derivatives developed, it was found that the formula above given required to be modified to some extent; but this is in no way surprising, as it is practically

impossible by analysis alone to arrive at a true conclusion as to the constitution of a compound of such high molecular weight, so unstable and so difficult to obtain pure.

Another green dye-stuff to which Hofmann directed his attention at this time was aldehyde green, produced by the action of aldehyde on rosaniline in presence of sulphuric acid whereby a blue colouring matter is formed, which is transformed into the green by the action of an aqueous solution of sodium thiosulphate. Lauth, apparently, was the first to produce the blue compound, in 1861, by subjecting a solution of rosaniline in alcohol, methyl alcohol, acetic acid, or acetone to the action of zinc chloride and other metallic salts, but the conversion of the blue into the green was accomplished by Cherpin in 1862. This was the first aniline green dye discovered (emeraldine, which was of no value, excepted), and was much used. Hofmann showed that aldehyde green contained sulphur, and assigned to it the composition indicated by the formula $C_{22}H_{27}N_3S_2O$, representing its formation by the following equation,

$$C_{20}H_{19}N_3 + C_2H_4O + 2H_2S = C_{22}H_{27}N_3S_2O$$

(*Ber.*, 1870, **3**, 761).

The next researches it will be most convenient to refer to, though not quite the next as to date, are those on the methyl violets; but, before considering these it may be mentioned that, in continuation of his researches on rosaniline derivatives, Hofmann, in 1873 (*Ber.*, **6**, 263), examined the violet obtained by Hobrecker by the action of benzyl chloride and methyl iodide on a solution of rosaniline in methyl alcohol, assigning to it the formula $C_{20}H_{16}(C_7H_7)_3N_3,CH_3I$.

Until long after the commencement of the coal-tar colour industry, chemists and experimenters directed their attention chiefly to aniline as a source of colouring matter; but in 1861 Lauth made some experiments on the product Hofmann obtained by acting with methyl iodide on aniline, which he described as methylaniline (*J. Chem. Soc.*, 1851, **3**, 296), but which recent researches have shown is a mixture of methylaniline and dimethylaniline, and by oxidising this he obtained violet colouring matters. Writing of these in 1867, Lauth says (*Laboratory*, 1867, 138), "The violets obtained from methylaniline possess a richness and purity which leave nothing to be desired . . . . Nevertheless, they were not adopted by manufacturers, who, indeed, at the time mentioned (1861) attached less importance to the beauty of a colour than to its permanence. In this latter respect the methylaniline violets do not excel, and, consequently, dyers would have nothing to do with them.

"Gradually, however, people have become accustomed to colours which fade on exposure to the solar rays . . . . Accordingly,

two years after the experiment made by myself, Dr. Hofmann succeeded in introducing these results." These remarks confirm those already made in reference to the gradual change in public opinion which led to the disregard of permanency in favour of brilliancy of colour.

Lauth further remarks that Hofmann's method of producing these colouring matters is the inverse of that proposed by him; the aniline being first converted into rosaniline and then methylated, whilst in his case this operation is first performed on the aniline.

It would, however, not have been practicable to carry out this process if the aniline had to be methylated with methyl iodide, because the base thus prepared would be too expensive to use as the raw material for the preparation of colouring matters. On account of the success of the Hofmann violet, experiments were made in France with the object of preparing methylaniline by a different and more economical process, so as to commercially produce Lauth's violet, and this was at that time considered especially desirable by some manufacturers, because the production of rosaniline in France was the monopoly of one house, and, therefore, derivatives of this colouring matter could not be economically made by others.

Eventually a successful process was discovered by M. Bardy, chemist to the firm of Poirier and Chapat, which consists in heating a mixture of aniline hydrochloride and methyl alcohol in a closed vessel to a high temperature. As is now well known, though not at first recognised, this process yields a mixture of mono- and di-methylaniline, consisting chiefly of the latter. Large quantities of methylated aniline were soon produced by this process, and used in the preparation of a violet colouring matter which was manufactured by Messrs. Poirier and Chapat, and called by them violet de Paris; a large block of this, weighing about 150 kilos., was exhibited in the Paris Exhibition of 1867 (?). The question then arose as to whether violet de Paris was identical or isomeric with methylrosaniline violet. Lauth considered that it was isomeric, and remarks: "Hofmann violets consist of methylated and ethylated rosaniline, and rosaniline is derived from a molecule of aniline and two molecules of toluidine. The violet de Paris, on the contrary, is produced from pure aniline free from toluidine, transformed into methylaniline, which is isomeric with toluidine. This methylaniline when oxidised is converted into the violet which may have a composition analogous to that of methylated rosaniline, but must differ from the latter in the same manner as methylaniline differs from toluidine."

Hofmann, being naturally interested in the relationship of these colouring matters, investigated the subject, and published his results

in 1873 (*Ber.*, **6**, 352). He first studied the conditions under which the colouring matter could be formed, showing that violet could be produced from pure dimethylaniline obtained by the distillation of trimethylphenylammonium hydrate; he also came to the conclusion from the examination of the colouring matter that it was a methyl-chlorhydrate of trimethylrosaniline.

$C_{20}H_{16}(CH_3)_3N_3 \cdot CH_3 \cdot Cl$, the base being
$C_{20}H_{16}(CH_3)_3N_3 \cdot CH_3 \cdot HO$.

He prepared iodine green by methylating this compound; also its leuco-compound.

This research must have been a very difficult and laborious piece of work, and although Hofmann's views as to the constitution of the dimethylaniline violet are not those now accepted, the accuracy of his work has not been impugned.

The long controversy which arose, soon after the time when Hofmann published his constitutional formula of rosaniline, as to the constitution of this colouring matter belongs to another chapter, and need not be referred to here.

Mention has already been made of the process for methylating aniline discovered by Bardy, which consisted in heating this base with hydrochloric acid and methyl alcohol. In 1871 Hofmann and Martius (*Ber.*, **4**, 742) made some experiments in reference to this method, working at higher temperatures than those usually employed (280—300°), and continuing the heating for a considerable time; in this way they obtained, besides methyl and dimethylaniline, a quantity of basic oil of higher boiling point, which eventually proved to be a complex mixture of methylated homologues of dimethylaniline, the products of an intramolecular change or atomic wandering.

These remarkable researches, like so many other purely scientific discoveries, ere many years had passed, were found to be of technical value in connection with the coal-tar colour industry, the cumidine that is so extensively used in the preparation of some of the diazo-colours being made by the method of Hofmann and Martius by heating xylidine with hydrochloric acid and methyl alcohol to a high temperature, about 300°.

Reverting once more to the early days of the coal-tar colour industry, I may now mention that the liquors from which mauve was precipitated were found to contain a red colouring matter which I succeeded in separating, although the amount obtainable was very small. This proved to be a beautiful dye producing crimson-red shades on silk. It was afterwards discovered that it could be produced by the oxidation of mauveine, and it was prepared in considerable quantity in this way, but was a very expensive product, and therefore

not very largely used. This dye-stuff was known first as "aniline pink," and afterwards as "safranine." In 1865 a colouring matter having the properties of safranine was produced without the use of mauveine by F. Duprey, by heating commercial aniline dissolved in acetic acid with lead nitrate. It was then obtained by acting on commercial aniline with nitrous acid and oxidising the mixture with arsenic acid. The colouring matter prepared in this way was examined by Hofmann and Geyger (*Ber.*, 1872, **5**, 531). They found it to be a base forming crystalline salts, among others a hydrochloride having the composition $C_{21}H_{21}N_4Cl$. As they found that it could not be produced from either aniline or paratoluidine, or a mixture of the two, but from orthotoluidine, they regarded it as a toluidine derivative. They also observed that the formula above given differs from that of mauveine by C_6H_4, making it appear possible that mauveine was phenyl-safranine. In the course of an investigation of the safranine, obtained by the oxidation of mauveine, of which I published an account some time after this (*J. Chem. Soc.*, 1879, **35**, 728), this substance was shown to form a hydrochloride represented by the formula $C_{20}H_{18}N_4$, which differs from that of the substance examined by Hofmann and Geyger by CH_2. On examining a commercial product manufactured by Messrs. Guinon and Co., of Lyons, from commercial aniline, both substances were found to be present, showing that two "safranines" existed, and I then also showed that probably a third was formed by the oxidation of pseudo-mauveine.

The formula of the safranine hydrochloride obtained from mauveine will be seen from the above to differ from mauveine by C_7H_6, so that the relationship of these substances is probably not of so simple a character as Hofmann and Geyger supposed, though, of course, C_7H_6 may simply mean displacement of hydrogen by tolyl. No doubt a great similarity exists between them, one proof of which is that their behaviour with sulphuric acid is analogous. This applies both to those referred to above and to the third compound since discovered.

In 1875 Hofmann made an examination of eosin (*Ber.*, **8**, 62), and thus disclosed to the world an important manufacturing secret, proving to demonstration the impossibility in these days of long hiding from chemists the nature of any substance, however complex. Eosin, as is well known, was the first representative of a new class of colouring matters which has since become of great importance.

Chrysoidine, which may fairly be termed the parent of an even more important class of colouring matters, the azo-dyes, the introduction of which marks a new era in this branch of chemistry, was investigated and publicly proclaimed by Hofmann in 1877 (*Ber.*, **10**, 213).

The colouring matter to which he next directed his attention was

pittacal, also called euppitonic acid, the interesting compound discovered by Reichenbach, as far back as 1835, produced from wood tar. Hofmann (*Ber.*, 1878, **11**, 1655; 1879, **12**, 1371 and 2216) was led to regard this substance as hexamethoxyrosolic acid, $C_{19}H_8(OCH_3)_6O_3$; on treating it with ammonia, he obtained a beautiful blue dye-stuff, thus,

$$C_{25}H_{26}O_9 + 3H_3N = C_{25}H_{31}N_3O_6O + 2OH_2,$$

which he regarded as hexamethoxypararosaniline,

$$C_{19}H_{13}(OCH_3)_6N_3O.$$

He then made the interesting discovery that the formation of pittacal, or euppitonic acid, from dimethylpyrogallate and dimethylmethylpyrogallate took place in a manner analogous to that in which pararosaniline was formed, thus,

$$\underset{\text{Aniline.}}{2\cdot C_6H_7N} + \underset{\text{Toluidine.}}{C_7H_9N} = \underset{\text{Pararosaniline.}}{C_{19}H_{17}N_3} + 3H_2$$

$$\underset{\text{Dimethyl pyrogallate.}}{2C_8H_{10}O_3} + \underset{\text{Dimethyl methyl-pyrogallate.}}{C_9H_{12}O_3} = \underset{\text{Pittacol or euppitonic acid.}}{C_{25}H_{26}O_9} + 3H_2,$$

comparisons which are of considerable interest.

Hofmann's last research in connection with the coal-tar colour industry was made as late as 1887, and related to the quinoline red prepared by Jacobson, in 1882, from coal-tar chinoline, benzotrichloride, and zinc chloride. Hofmann, however, found that a better yield of colouring matter, either identical or isomeric with Jacobson's, is obtained by using a mixture of isoquinoline and quinaldine. Like quinoline blue or cyanine, the colour is not a fast one, which, as previously mentioned, is remarkable, considering the stability of quinoline itself. It is a somewhat remarkable coincidence that this should have been the last research Hofmann made on the coal-tar colours, as chinoline (or leucoline) was one of the two substances he gave an account of in his first investigation published in 1843, when 30 years of age.

Excepting what is said of pittacal, and the brief reference to eosin and chrysoidine, the foregoing account has reference only to what may be termed aniline colours, the great chapter on the history of technical chemistry, with which Hofmann's name is indissolubly linked.

An entirely new chapter in coal-tar chemistry opens in 1868, when Graebe and Liebermann (in connection with their researches on quinones) made their great discovery of the artificial formation of alizarin from anthracene. They patented their process in Germany

in October, and in this country on December 18th of that year. Their process, it is well known, consisted in producing dibromanthraquinone, either by brominating anthraquinone in sealed tubes, or by oxidising tetrabromanthracene, and subsequently displacing bromine by hydroxyl, by fusion with alkali.

This discovery for the first time of a method of obtaining a vegetable colouring matter artificially was, however, as it stood, of no practical value, as such a process could not be carried out on a large scale.

But why should this be mentioned here? It may seem that any reference to the alizarin industry is out of place in a notice designed to elucidate Hofmann's influence on the development of our knowledge of products derived from coal-tar, as he apparently never took any part in the investigation of anthracene derivatives. Yet it is to his influence that I can trace back my interest in the subject, for, as mentioned early in this account, the very first subject in research which he suggested to me was to prepare a nitro-compound and a base from anthracene. In the course of this work I not only became thoroughly acquainted with this hydrocarbon, but also prepared anthraquinone and other derivatives of it, and consequently was, perhaps, more fully prepared than any other chemist of the day to appreciate the discovery of the relationship of alizarin to anthracene, and was naturally impelled at once to attempt to adapt it to practical requirements. It is more than probable that I should have paid but ordinary attention to Graebe and Liebermann's work had I not possessed an early attachment to anthracene, and I am glad to recognise that I owe this to the knowledge and insight of my great master.

Being aware of the importance of alizarin as a colouring matter, and having some quantity of anthracene and anthraquinone left over from my experiments at the Royal College of Chemistry, I commenced to experiment on the formation of this substance, with the object of finding a process by which bromine might be dispensed with.

I knew of the remarkable stability of anthraquinone: that it could be crystallised from concentrated sulphuric acid without undergoing change, and that in making a combustion of it, if the operation were at all hurried, part of the anthraquinone would pass through the heated tube, and condense at the cool end unaltered.

Moreover, not long before I commenced to work at the artificial formation of alizarin, namely, in 1867, Wurtz and Kekulé had shown that when benzenesulphonic acid was heated with potassium hydrate, it gave phenate and sulphite; and Dusart had also found that naphthalenedisulphonic acid was in like manner converted into a dihydroxynaphthalene; so that it appeared probable that if a disulph-

onic acid of anthraquinone could be obtained, it would be possible to convert it by the new reaction into alizarin.

Anthraquinone was therefore heated with oil of vitriol more and more strongly, until the boiling point was nearly reached, as I was determined either to obtain a sulphonic acid or destroy the anthraquinone; and at last it was found that the anthraquinone had disappeared, yielding a product which was soluble in water. After the excess of sulphuric acid had been removed in the usual way with barium carbonate, the product was fused with caustic alkali, and to my delight it changed first to violet, and then became black from the intensity of its colour. On dissolving the melt, a beautiful purple solution was obtained, which gave a yellow precipitate when acidified, and on examination this was found to dye mordanted cloth like garancine.

On the 20th of May (1869) I sent dyed patterns to my friend Mr. Robert Hogg, of Glasgow, who had a very large experience in reference to madder and garancine, and also of the coal-tar colours from the days of the mauve dye, whose opinion I valued very much in all practical matters connected with dye-stuffs, especially from a commercial point of view, and he was very favourably impressed with the results I had obtained. This process, however, was not patented until June 26. (About the same time as I discovered this process, Graebe, Liebermann, and Caro quite independently arrived at the same result in Germany.) This process has proved the most permanently important one yet discovered, and is the one still universally used. I was also fortunate enough to discover a second process, which was of great value in the early days of the industry. but is not in use now so far as I know. It consisted in the use of dichloranthracene as the starting point, instead of anthraquinone. This substance was found to readily afford a sulphonic acid, which could be easily changed into anthraquinonesulphonic acid, either by oxidising its solution with manganese dioxide or more simply by heating it with sulphuric acid. This process was patented in November, 1869.

After discovering processes by which artificial alizarin could be produced, the technical value of the artificially prepared dye-stuff had to be ascertained. Experiments were soon made by the calico printers, as no new processes had to be discovered for the application of this colouring matter, those in use for madder and garancine being suitable. Turkey-red dyers also experimented with it, but some were not so successful as others, for reasons easily understood afterwards, when the properties of anthrapurpurine, which it contained, were better known.

The subject of price, however, was the important question, because

this product had to compete with those already in the market, namely, madder and garancine, and therefore high prices could not be obtained as in the case of a new dye.

Before this could be settled, the first thing necessary was to get a supply of anthracene. This substance was not at this date separated by the tar distillers, there being no use for it; many of them, in fact, knew nothing of its existence, and the question as to whether it could be obtained in sufficient quantity and at a sufficiently low price had to be settled.

But experiments I had made on the small scale, on the distillation of soft pitch, at the Royal College of Chemistry, gave me confidence, and my brother and I entered into the matter with great energy.* At first we prepared anthracene by distilling pitch ourselves, and thought of using this as a source of this hydrocarbon on an extensive scale, as we felt it was capable of yielding a considerable supply. We knew, however, that it could also be obtained from the last runnings of the tar stills, from which it crystallised on cooling. My brother, therefore, visited nearly all the tar works in the kingdom, and showed the distillers how to separate the anthracene, promising to take all they could make, and in this way a sufficient and rapidly increasing supply for our requirements was soon obtained of all sorts of qualities, some being not much thicker than pea soup, from the imperfect way in which it was drained. Very few tar distillers in those days had hydraulic presses, such as are now used, with which they could free the solid from the excess of oil. The value of the anthracene was estimated by washing with carbon bisulphide, afterwards alcohol was used, but for our own purposes we all along used an anthraquinone test. This method was afterwards worked out more perfectly on the Continent, and made a practical test for both the buyer and seller; but at the time I am writing of tar distillers were not sufficiently educated in such matters to use any but very simple tests.

The purification of the anthracene sufficiently for our purpose had then to be worked out, and in doing this I found out a curious fact, namely, that when distilled with caustic potash it was much improved in quality—considerably more so than when distilled either alone or with caustic soda. And potash distilled anthracene was especially necessary when dichloranthracene had to be prepared, as it yielded a well-crystallised, easily purified product, whereas anthracene which had been distilled, either alone or with caustic soda, gave a badly-crystallised, sticky product, which was very difficult to purify.

On examining into the action of caustic potash on anthracene, it was

* My father, to whose great kindness I was so much indebted, died in 1864, so that our firm then consisted only of my brother and myself.

found that if, after the anthracene had been distilled off, the residue was freed from akali by washing, and then distilled, a substance very like anthracene was obtained, which Graebe subsequently found to be the nitrogenous compound now known as *carbazol*. It is by means of caustic potash that this substance is now separated from crude anthracene, and the process is still used to a large extent to improve the quality of anthracene. All the anthracene we used at Greenford Green was treated in this manner.

The purification of the anthraquinone was at first effected by sublimation, followed by crystallisation. A good deal of difficulty was experienced in the conversion of this substance into its sulphonic acid, however, and at the high temperature at which combination took place, the formation of steam from the water produced at the same time led to considerable quantities of the anthraquinone becoming sublimed, which, although not lost, yet was a source of trouble in various ways. The means of overcoming this difficulty was to use fuming sulphuric acid, with which anthraquinone combined at a much lower temperature, but the only acid of the kind then made was the old-fashioned Nordhausen acid. We imported a quantity of this, and, of course, found it to work satisfactorily, but the difficulties and expense connected with the carriage and transport of this substance on account of its dangerous nature—supplied as it then was in large earthenware bottles—made it unsuitable for use in this country.

The artificial alizarin we first made was produced by the anthraquinone process, the method still used for its manufacture, but the difficulty in preparing the sulphonic acid in those early days just referred to caused us to turn our attention to the second process I had discovered, in which dichloranthracene was used. After finding out the best way of preparing the substance, our difficulties in reference to the sulphonic acid vanished, as dichloranthracene dissolves easily in hot ordinary oil of vitriol, producing dichloranthracenedisulphonic acid; on continued heating this acid oxidises, hydrogen chloride and sulphur dioxide being evolved and anthraquinonedisulphonic acid formed. Without this process, the manufacture of artificial alizarin in this country could not have been carried on with much success in the early days of its manufacture.

The conversion of the anthraquinonesulphonic acids into colouring matter by treatment with caustic alkali at a high temperature at first presented many difficulties when carried out on the large scale. Our earliest experiments were made by heating the mixture in iron trays in a large air bath. Mixtures of caustic potash and caustic soda were also experimented with instead of caustic soda alone. Then the mixture was placed in a revolving cylinder, heated in an

air bath, small cannon balls being put into the cylinder to mix the product. But all these methods were only partially successful, the percentage of colouring matter produced not being so high as it should have been. At last heating in a very strong iron boiler under pressure was resorted to, and by adopting this method—which is now that universally used—we obtained a satisfactory result.

From the experiments we made in 1869 we felt pretty confident that artificial alizarin could be made at a price to compete with madder and garancine, and before the end of the year we had produced 1 ton of this colouring matter in the form of paste, in 1870 40 tons, and in 1871 220 tons, and so on in increasing quantities year by year.

The colouring matter produced from dichloranthracene was chiefly anthrapurpurin containing a little flavopurpurine. Theoretically it should have consisted of these products only, but owing to the occurrence of a secondary action, which I need not refer to here (see *Lectures Soc. Arts*, May 30th, 1879), it also contained alizarin, which we sometimes separated when required for dyeing purples. This colouring matter yielded a shade of colour which answered most of the requirements of the consumers for some time, as it was chiefly used by the Turkey-red dyers, and the supply being limited, it was often used in combination with garancine, as in this way more brilliant reds could be obtained than when using garancine alone, though, of course, the use of the artificial colouring matter alone yielded still clearer and more fiery shades.

Dichloranthracene was afterwards found to yield a monosulphonic acid when treated with sulphuric acid, provided the temperature were kept low and the amount of acid limited; and when oxidised with manganese peroxide or other oxidising agent, this yielded anthraquinonemonosulphonic acid, from which alizarin alone could be obtained. But the properties of dichloranthracenemonosulphonic acid were such, and the technical difficulties of carrying out the process so considerable, that it was never used very successfully. Moreover, by this time, fuming sulphuric acid had come into use, and anthraquinonemonosulphonic acid could be more readily produced directly from anthraquinone. As we had been successful in producing artificial alizarin, others did not run much risk in following our lead; yet, up to the end of 1870, the Greenford Green Works were the only ones producing artificial alizarin. German manufacturers then began to make it, first in small and then in increasing quantities, but until the end of 1873 there was scarcely any competition with our colouring matter in this country.

From the foregoing, it is seen that, as in the case of the aniline colours, all the pioneering work connected with the foundation and

establishment of this branch of the coal-tar colour industry was also done in this country.

For the due development of this industry, it was necessary not only to attend to technical processes, but also to carry on scientific research in connection with it. Early in 1870, I had the honour of bringing before this Society an account of some experiments on the formation of the colouring matter obtained from the sulphonic acids of anthraquinone, showing that it contained alizarin possessed of both the chemical and optical properties of that obtained from madder root. At the same time, attention was directed to the existence of a second colouring matter, yielding reds more scarlet and purples of a bluer shade than alizarin (*J. Chem. Soc.*, 1870, **23**, 133). This second colouring matter was afterwards made the subject of further investigation, and shown to be an isomer of purpurin; it was therefore called *anthrapurpurin* (*J. Chem. Soc.*, 1872, **25**, 659, and 1873, **26**, 425). Dichlor- and dibrom-anthracene and their disulphonic acids, &c., were also investigated. Anthraflavic acid, discovered by Schunck in some secondary products sent to him from my works, was made the subject of two researches; in the first of these, this compound was shown to be an isomer of alizarin, and not to contain C_{15}, as supposed by its discoverer. In the second, the sublimed acid was examined and found to be identical with the unsublimed; it was also shown that when fused with alkali it did not yield alizarin, as stated by Schunck, but a colouring matter yielding orange-red colours with alumina mordants. This, Schunck and Roemer, some time afterwards showed to be another isomer of purpurin which was named by them flavopurpurin.

In this investigation, anthraflavic acid was found to yield a diacetyl and dibenzoyl derivative, which was evidence that it contained two hydroxyl groups like alizarin (*J. Chem. Soc.*, 1873, **26**, 19). Later on, an investigation was made on the formation of anthrapurpurin, proving that, as in the case of flavopurpurin, the formation of the colouring matter from the disulphonic acid of anthraquinone is preceded by that of a dihydroxy-derivative, also an isomer of alizarin, now known as *isoanthraflavic acid*, which, when heated with caustic alkali, is partially oxidised into anthrapurpurin and partially reduced (*J. Chem. Soc.*, 1876, i, **29**, 851). Besides these, the formation of bromalizarin (*J. Chem. Soc.*, 1874, **27**, 401), of β-nitroalizarin (*J. Chem. Soc.*, 1876, ii, **30**, 578), of anthrapurpuramide (*J. Chem. Soc.*, 1878, **33**, 216), and of the dibromanthraquinones discovered by Graebe and Liebermann and the colouring matters obtainable from them, were investigated (*J. Chem. Soc.*, 1880, **37**, 554). Much work has also been done in reference to this industry by Graebe and Liebermann and other investigators.

The manufacture of artificial alizarin in Germany has been almost

entirely confined to the anthraquinone process, fuming sulphuric acid being used in the preparation of the sulphonic acids. For this purpose very strong acid, containing about 40 per cent. of anhydride, was made from Nordhausen acid, and used until the process of making sulphuric anhydride by decomposing sulphuric acid into sulphurous oxide, oxygen, and water, and recombining the two former, was introduced.

After being engaged in the coal-tar colour industry for 18 years, my connection with it, technically, came to an end in 1874, when the alizarin industry had been well established and was rapidly extending.

On looking back over the period, it is of interest to see the wonderful progress the industry had made up to that time—a progress which was going on by leaps and bounds. I have no statistics connected with the precise period, but four years afterwards, namely in 1878—with the kind assistance of Dr. Caro—an estimate of the value of the colours produced during that year was obtained, at a time when the industry had just passed its majority and was 22 years old. The sum amounted to £3,150,000. (See *Jour. Soc. Arts.*, May 30, 1879.) Of its present position, it is very difficult to speak. Certainly its progress has been very great since 1878; but chiefly owing to the scientific skill bestowed upon the production of the colouring matters, their cost has been greatly diminished, so that I understand rosaniline hydrochloride, which once was worth about £3 3*s.* per ounce, may now be purchased at 2*s.* 9*d.* per lb., and aniline at less than 6*d.* per lb.

* * * * * * *

During the early days of the coal-tar colour industry, the complaint was made that the prosecution of purely scientific chemistry was being injured by its influence, as chemists were everywhere experimenting with aniline and other products, with objects of a more selfish than scientific character. It is probable that there was some truth in this for a time, but it was not long before a welcome change set in, and the work carried on in relation to this industry was soon conducted in a scientific spirit, even when the result sought for was expected to be of technical, as well as where it was expected to be of scientific, value. But the amount of work carried on from the latter point of view increased more and more, as interesting questions connected with the colouring matters and the methods by which they were produced presented themselves to chemists, and now if we look back and consider what has been accomplished, we find that this industry has directly and indirectly had a most marvellous influence on the advancement of

chemical science, especially that part of it relating to the aromatic series of compounds. No other industry in existence can at all be compared with it from this point of view. This has arisen from a variety of circumstances, one of which is that it has not been carried on by the rule of thumb method which has been so common in other cases. Again, as it has utilized the discoveries of chemists, it has handed back to them in return new products which they could not have obtained without its aid, and these have served as materials for still more advanced work: this kind of exchange, indeed, has been going on so repeatedly, that products formerly of the rarest and most complex character are now quite common substances in the coal-tar colour works.

We knew that aniline was at first a rare substance, and when it was afterwards proposed to use ethyl and methyl iodides in the preparation of ordinary dye-stuffs, it seemed incredible that such substances could be introduced for such a purpose as already mentioned, substances which were but rarely met with even in chemical laboratories: but what are these compared with the substances now in use? —their names would be too numerous to mention. One of the most striking facts connected with this industry is the remarkably rapid way in which it has utilized new discoveries which have often been no sooner made than they have been practically applied. This no doubt arises from the fact that an ever increasing army of highly trained and highly gifted chemists are engaged in the industry, especially on the Continent, provided with splendid laboratories, libraries of scientific works and all the most advanced appliances required in scientific research; and the members of this army are not only making discoveries themselves and applying them, but are always on the alert to make the discoveries of others subservient to the industry.

As I have already mentioned, when this industry was first instituted, organic chemistry was comparatively in its infancy, especially if we regard it from our present standpoint. Kekulé had not then brought forward his remarkable benzene theory, and after he had done so its bearings required much elucidation before their importance was well understood. Only solid toluidine was known, orthotoluidine not having been discovered, although it was constantly present in the high boiling aniline used in making rosaniline; but now the facts connected with the ortho-, meta-, and para-position in substances containing the benzene nucleus, or of the α- and β-positions in the naphthalene series, are among the most important to be considered in the manufacture of colouring matters; in fact, this industry has done more to accentuate the importance and character of these positions than any other kind of experimental work.

Although at the commencement of the industry a good deal of work of a purely experimental character had to be done, nevertheless, from the first it was carried out on scientific lines, and this characteristic increased very rapidly, as is seen by the early date at which mauve and magenta were obtained in the pure crystallised condition: it was at this period, as previously stated, that Hofmann commenced his researches on rosaniline and its derivatives, and on other colouring matters, and these researches, taken with those of others, bear out the observations which have just been made. In looking over the work of Hofmann in this field, all who have had experience in the investigation of the subjects he undertook must realise that they presented no ordinary difficulties, especially as for some time he had nothing to guide him in his conclusions but the analytical results. In the early days of organic chemistry, it is well known that on finding colouring matters in the products they were examining, chemists usually regarded them as impurities, and the use of animal charcoal and other means were resorted to for the purpose of getting rid of them; and those who undertook the examination of colouring matters themselves were considered as bold men, and not likely to get much result from their labour. Doubtless, there was much truth in this. Hofmann, however, *was a bold man*, and not one to be daunted, but rather inspired, by difficulties; and from his results we see how great his success was in this department of chemistry, some of his work proving to be of direct practical value, whilst other parts possessed important bearings both on the practical and scientific development of this subject. His researches on colouring matters extended over a quarter of a century, commencing in 1862 with rosaniline, and ending in 1887 with quinoline red; and during that period there were but few years in which he did not produce one or more investigations, either related to colouring matters or the products connected with their production.

It will be obvious from what has been said, how Hofmann's early work—after that of Faraday, Unverdorben, Runge, Fritzsche, Mitscherlich, and Zinin—continued to pave the way for the introduction of the coal-tar colour industry, also how the important influence he exercised on the training of his students led in the same direction. I especially refer to Mansfield, who did such valuable work on coal-tar, and Nicholson, whose chemical education under Hofmann was such an important preparation for the work he undertook in after years on rosaniline and its derivatives; and if I may speak for myself, I can only say how much I owe to Hofmann's training, which fitted me to carry out the work which fell to my lot in connection with the introduction and development of this industry. Then if we further consider the importance of the beautiful researches Hofmann

made, some of which yielded practical results, throwing fresh light on the nature of the colouring matters and products related to them which were obtained as time went on, some idea may be formed of the contributions made by Hofmann and his school to the coal-tar colour industry.

And yet we must bear in mind that his work in this department of chemistry represents but a small part of all that he accomplished—indeed, the amount of scientific work he did was something marvellous.

Notes on Hofmann's Scientific Work.

By Henry E. Armstrong.

"The eye may rest with complacency upon the simple beauty of the law which governs the construction of the bodies belonging to the type of ammonia."

The accounts of Hofmann given by Lord Playfair, Sir Frederick Abel and Dr. Perkin are of the greatest value, as affording us the means of knowing the conditions under which he was placed in this country, as well as of understanding the man and the marvellous influence he exercised on all who enjoyed the advantage of working with him. Dr. Perkin's autobiographical reminiscences, and his frequent references to others who laboured successfully in the same field with himself—who, like himself, had been pupils under Hofmann—are a striking testimony to the value of the training imparted by the great master; and this has received even fuller recognition from those who were influenced only at a distance, notably in Dr. Caro's masterly monograph published in 1892 by our German colleagues, as well as in the address delivered by Professor Tiemann shortly after Hofmann's death.

When we take into account the state of knowledge at the present day, and the conditions under which we now work, the contrast which the pictures painted by our three essayists present is indeed a striking one. Starting in times of what may fairly be called rudimentary civilisation, when chemistry could scarcely be called a science, so incomplete and uncoordinated was our knowledge, even ere 50 years are lapsed, we find ourselves in an age of luxurious material profusion, equipped with an extraordinary wealth of new and potent methods of inquiry; methods which have already enabled us to penetrate deeply into the inner mysteries of nature in a manner which must have been altogether inconceivable in Hofmann's early days—for, as Dr. Perkin tells us, those were times when the constitution of compounds was worked out on simple arithmetical lines.

And the progress of the industry which it will ever be the proud

boast of the Hofmann school to have founded is even more marvellous; no fairy tale can match its wonders. Moreover, as its biographers, Perkin and Caro—the two men who, with Hofmann and Nicholson, have done most to develop it—imply, the doctrine that action and reaction are equal and opposite was never more strikingly illustrated, the effect produced by the translation into practice of the results of inquiries undertaken with purely scientific objects in view having almost invariably been followed within a short time by the fullest repayment, in the form either of materials needed by the scientific inquirer or of new problems for investigation, and that apart from the encouragement afforded to workers by the prospect of material rewards. The example thus set has spread to other industries. All who have studied the question are agreed that it is impossible to overrate the share borne by Hofmann, both directly and indirectly, in promoting such progress; to repeat words the present writer used on the occasion of the memorial meeting, we are indebted to him probably to a far greater extent than we shall ever be able to realise, and he will undoubtedly rank among the chemists of the Victorian era as second only to his great master, Liebig—to whom, indeed, he bore the greatest resemblance, in being possessed of most unusual powers of influencing others and of inciting them to work.

Hofmann's own prescience in appraising the national value of science was remarkable, and it is clear that the influence he exercised in introducing scientific method into industry was in no sense accidental, but the considered expression of innate convictions. This is clearly shown by his "Remarks on the Importance of Cultivating Experimental Science in a National Point of View," the substance of a lecture delivered at one of the evening meetings of the College which is appended to the preface to the volume of *Reports of the Royal College of Chemistry and Researches conducted in the Laboratories in the Years* 1845–47, published in 1849. In concluding this he says—

"My principal object, on the present occasion, has been to insist upon the importance of cultivating natural science in its bearings upon the whole mechanism of society, as the mainspring both of individual and national prosperity; and I cannot conclude more appropriately than in the words of the venerable Humboldt, one of the most distinguished philosophers of the present age: 'An equal appreciation of all parts of natural knowledge is an especial requirement of the present epoch, in which the material wealth and the increasing prosperity of nations are in a great measure based on a more enlightened employment of natural products and forces. The most superficial glance at the present condition of European states shows that those which linger in the race cannot hope to escape the partial diminution, and perhaps the final annihilation of their resources. It is with nations as with nature, which, according to a happy expression of Goethe, knows no pause in

increasing movement, development, and production, attaching a curse to standing still.

"'Those states which remain behind in general industrial activity, in the selection and preparation of natural substances, in the application of mechanics and chemistry, and in which a due appreciation of such activity fails to pervade all classes, must see their prosperity diminish, and that the more rapidly as neighbouring states are meanwhile advancing, both in science and in the industrial arts, with, as it were, renewed and youthful vigour.' —*Cosmos*."

A suggestive paragraph occurs in Lord Playfair's notice which may well be read in connection with this quotation from Humboldt. It is a grave question whether Hofmann was not led to accept the invitation to quit this country and return to his fatherland because he was able to fathom the hopelessness of the situation here, and foresaw—as events have proved—that Humboldt's countrymen alone could appreciate his warning. Perhaps he felt our insular conservatism to be beyond even his powers, and understood that men like Perkin and Nicholson had but strayed into industrial pursuits, and were in no sense representatives of the English character. Whatever may be the explanation, it cannot be denied that the higher chemical industries have rapidly retrograded in this country almost from the moment of Hofmann's departure; and it can scarcely be doubted that had he continued to exert his unrivalled personal influence, our manufacturers would long ere this have been persuaded to follow the methods so successfully adopted by others, and to fully avail themselves of the services of well trained scientific assistants.

Seeing that no scientific man has ever more directly influenced industry, it is interesting to note that, at the very outset of his career, Hofmann entered into direct and intimate relations with industrial workers; in fact, in his first paper he expresses his indebtedness to his friend Ernest Sell, in whose asphalt works at Offenbach, on the Main, the crude basic oil he used in his research was separated from Belgian tar; the association thus established appears to have had a determinative influence on his whole life. This fact is of no slight importance.

In order to understand Hofmann's services to science, it is necessary to consider his work as a whole, not merely that relating to colours, which after all is to be regarded as but a single episode in a remarkably varied career. It is indeed remarkable how much of what is now the framework of our science is traceable to his labours. In order that this may be realised, it will often be desirable to quote his own clear and graphic statements, sometimes at considerable length; their style is at all times characteristic; and they are of considerable historical interest, as showing how discoveries of such

fundamental importance were arrived at and that devotion to the highest scientific aims is compatible with the existence of the greatest possible interest, and even active participation, in industrial pursuits. Hofmann may be said, indeed, to have been a technical chemist *par excellence*, and his school the type of a true technical school; it is the infusion of the spirit in which he worked into German chemical industry that undoubtedly has led this to achieve such marvellous results, especially during the past five and twenty years.

* * * * *

His first investigation was published in 1843, in *Liebig's Annalen* (**47**, 37—87), under the title "Chemische Untersuchung der organischen Basen im Steinkohlentheeröl."* He concludes with the warmest expression of thanks to his teacher—Professor Liebig—in whose laboratory the work had been executed. With remarkably few exceptions, all his subsequent investigations are clearly the logical outcome of this his earliest inquiry. Seldom has an original worker proved so true to his first love, but seldom has a worker fallen on a theme permitting of such infinite extension.

We not only find the key to his later work in this paper. The power of exposition of which he became so great a master is already beginning to show itself, although the highly polished diction and cosmopolitan wealth of expression which so distinguished his later writings are not yet in evidence; these were probably in part derived from his philological training—of which Lord Playfair reminds us—but doubtless also largely the outcome of inherent qualities of mind, reflections of the inner man. But finish of style and completeness are equally apparent in the work itself, and it is obvious that the care which he devoted to the illustration of his lectures, and the insistence on the purification of any substance to be dealt with in an investigation, to which Dr. Perkin refers, were also but expressions of his innate character.

The finished style of his early work, which presumably was entirely his own, appears all the more remarkable when we bear in mind that—as all who were associated with him tell us—he was himself a most awkward manipulator; and that the success he afterwards achieved was due to his extraordinary power of inciting others to work, and to the remarkable judgment he displayed in selecting helpers gifted with powers of experimenting with which himself he was so indifferently endowed. And the manner in which he returned his thanks was equally striking and characteristic; indeed, if the complimentary references in his papers to those who at various times

* The same paper was subsequently published in the *Philosophical Magazine*, 1844, **24**, 115, &c., under the title "A Chemical Investigation of the Organic Bases contained in Coal-gas Naphtha."

assisted him were collected, they alone would afford an interesting and matchless record of his diplomatic talents and courtly manners.

His work on coal tar was published less than ten years after Runge (1834) had discovered in that substance *kyanol*, *leukol*, *pyrrol* and *carbolic acid*, no one of which he analysed, however; but Laurent, shortly before Hofmann's work was carried out, had ascertained the composition of carbolic acid and had termed it phenyl hydrate. Judging from his own statement, Hofmann appears to have been led to undertake the investigation of Runge's kyanol and leukol because they were described as basic substances, at a time when such substances were attracting special attention in Liebig's laboratory, and he only refers to Fritzsche's *anilin*, Unverdorben's *krystallin* and Zinin's *benzidam* after describing his work on kyanol. According to Professor Tiemann, however, Liebig had proposed to him to clear up the relationship of *anilin*, *benzidam* and *krystallin*, which Erdmann had suggested were identical, and Professor Tiemann leads us to suppose that the examination of Runge's leukol was incidental to this inquiry, but of this there is no mention in the paper.

Hofmann separated kyanol from leukol—he obtained only about 1 per cent. of basic oil from the heavy tar oil—by distillation, but purified it by conversion into the oxalate, which he recrystallised from absolute alcohol. He fully described its properties, several of its salts, and its more characteristic actions. At the close of the paper, he describes a number of important observations on its behaviour with a mixture of muriatic acid and potassium chlorate—an agent already applied by Fritzsche to *anilin*—obtaining chloranil, which Erdmann had previously prepared from isatin and chlorine; *benzidam* was shown to behave similarly. By the action of chlorine, he obtained products identical with substances previously prepared by Erdmann from indigo, one of which he recognised as trichlorinated phenol, Laurent's chlorophenissic acid. Nitric acid, in like manner, was found to produce picric acid. Important use was made of these observations: the simultaneous production of phenol and *kyanol* on distilling coal, and the formation of the same chlorinated and nitrated compounds from both, leading him, in fact, to regard them as related compounds, and accepting Laurent's view that carbolic acid was the hydrate of the oxide of an organic radicle, $C_{12}H_{10}$, *phen*, he represented *kyanol* as the amide of the same radicle—as *phenamide*, $C_{12}H_{10} + N_2H_4$. Futile attempts to convert phenol into *kyanol*, made from this point of view, are then referred to.*

* A short time afterwards, however, Laurent and Hofmann succeeded in effecting the conversion. The note on the subject which Laurent communicated to the French Academy on December 26, 1843 (*Compt. rend.*, **17**, 1366) has apparently not received the attention it deserves; no better evidence could be given of the

The clearness of Hofmann's theoretical conceptions at this time does not appear to have been sufficiently recognised; yet it is certain that he did far more than merely discover aniline in coal tar and prove its identity with certain products from other sources: he at once saw that he had discovered not a substance only, but a problem. Moreover, after objecting to the name *kyanol*, because it was made up of words from two languages, one of which was already appropriated; and also to *anilin* and *benzidam* as defining its relation to certain classes of compounds, and therefore undesirable, as it could

extent to which he was in advance of his time, even as regards the constitution of bases like aniline. Laurent writes as follows:—

Sur un nouveau mode de formation de l'aniline. M. Aug. Laurent.—J'ai entrepris avec M. Hofmann quelques recherches ayant pour but de préparer l'aniline. Je pense que les idées qui nous ont servi de guide dans ce travail pourront intéresser les chimistes.

L'aniline pouvant être considérée comme l'amide de l'acide phénique,

Acide phénique ..... $C_{24}H_{12}O_2$
Aniline ..... $C_{24}H_{10},H_4Az_2$.

Nous pouvions espérer de transformer l'acide en amide, en faisant réagir l'ammoniaque sur lui. On devait avoir:

$$C_{24}H_{12}O_2 + H_6Az_2 = C_{24}H_{14}Az_2 + H_4O_2.$$

Comme le phénate d'ammonium se décompose très-facilement par la distillation en acide et en ammoniaque, nous avons d'abord essayé de faire réagir ces deux corps à une température rouge, mais sans avoir l'espoir de réussir. En voici la raison, telle que je l'ai donné a M. Liebig, qui assistait à notre expérience. Supposons que l'ammoniaque puisse réduire, à une température rouge, l'acide phénique et former de l'eau, on devra obtenir, si les idées que j'ai développées sur la substitution sont vraies, non de l'aniline, mais un composé isomère. En effet, la formule rationelle de l'acide phénique doit se représenter par

	$C_{24}H_{12} + O_2$
Ajoutant l'ammoniaque	$H_4H_2Az_2$
	H_4
Retranchant	O_2
	$C_{24}H_{12} + H_2Az_2$

c'est-à-dire, de l'acide phénique dont les deux atomes d'oxygène sont remplacés par deux atomes d'imide.

Or, l'aniline ne renferme pas d'imide, mais de l'amide, ce qui se demontre très-facilement par les deux méthodes qui servent à la préparer.

Première Méthode.

Le phéne (benzène) = $C_{24}H_{12}$,

il donne avec l'acide nitrique,

Le nitrophénase = $C_{24}H_{10}(Az_2O_4)$,

celui-ci donne avec l'hydrogène sulfuré, en remplaçant O_4 par H_4,

L'amidophénase (aniline) = $C_{24}H_{10}(Az_2H_4)$.

be obtained from so many sources: he suggested the selection of *krystallin* from among the names proposed, *until it should be possible to establish by experiment the scientific name phenamide.* Why he so soon afterwards adopted the name aniline is not evident: no other appears in any of his subsequent papers, except phenylamine when theoretical relations are under discussion.

Even with the evidence afforded by his first paper alone before us, it cannot be said that Hofmann was not a theorist; it is true that he took little part in the later developments of chemical theory, but it is equally clear on studying his early work that from the very beginning, after he had grasped the fact that phenol and aniline bore a close genetic relation to each other, the whole of his work was based on, and consistently guided by, clear theoretical conceptions. We must remember that during many years he devoted himself to the study of compounds of a very simple type—the amines—and being moulded on such a model, his style naturally became a simple one.

* * * * *

Deuxième Méthode.

La formule rationnelle de l'acide anthranilique doit se représenter par

$$C_4C_{24}H_{10}(Az_2H_4) + O_4$$

En enlevant.... $C_4 \qquad O_4$

On obtient encore l'aniline .... $C_{24}H_{10}(Az_2H_4)$

J'ajoutai à M. Liebig que nous n'aurions pas réussir que si le phénate d'ammonium eût pu résister à une plus haute température.

En effet, si le phénate d'ammonium ne pouvait se décomposer qu'à 300 degrés, par exemple, cette température serait peut-être suffisante pour permettre à l'hydrogène de l'ammonium de se combiner avec l'oxygène. On aurait alors

Phénate d'ammonium..... $C_{24}H_{12}(H_8Az_2) + O_2$

Retranchant..... $H_4 \qquad O_2$

Il reste de l'aniline ..... $C_{24}H_{10}(H_4Az_2)$

Notre expérience ne nous donna aucune résultat. L'aniline et l'ammoniaque passèrent dans un tube chauffé au rouge sans se décompose mutuellement.

Nous avons alors renfermé du phénate d'ammonium dans un tube de verre très-épais que nous avons fermé à la lampe, et nous l'avons exposé pendant quelques instants, dans un bain d'huile, à la température de 260 degrés environ. Après le refroidissement nous avons trouvé des traces d'aniline dans le produit.

Nous avons recommencé l'expérience, mais nous avons placé le tube dans un four dont la température pouvait varier de 100 à 300 degrés, et nous l'y avons laissé pendant deux à trois semaines. En brisant le tube, nous y avons trouvé une assez grande quantité d'aniline. Il est bien évident que la réaction est due à la décomposition du phénate d'ammonium, et non à la décomposition mutuelle de l'acide phénique et de l'ammoniaque, puisque ces deux corps ne réagissent pas l'un sur l'autre à une température rouge.

On entrevoit la possibilité de faire de la quinine, de la morphine, &c., si l'on parvient à découvrir des composés correspondant à l'acide phénique.

The investigation published in 1845, under the title "On the Metamorphoses of Indigo. Production of Organic Bases which contain Chlorine and Bromine" (*Chem. Soc. Memoirs*, February, 1845, **2**, 266), must be regarded as the real starting point in Hofmann's scientific career. To this is appended the following memorable postscript—

"I have had the pleasure of witnessing the care and accuracy with which the author of this paper has proceeded in making his observations and establishing his facts. It appears to me that he has produced a definite and irrefragable proof that the chemical character of a compound does not depend, as the electro-chemical theory supposes, upon the *nature* of the elements it contains, but solely on the manner of their grouping."—JUSTUS LIEBIG.

Admirable in conception, execution and clearness of statement, this memoir is full of interest, owing to its importance in the history of our science. The work was brought forward at a time when the contest was at its height between the substitution theory and the electro-chemical dualistic theory of Berzelius—the theory that every compound is formed of two constituents, one electro-positive the other electro-negative. Only eight years before, Laurent—we read—had laid down the following law—

"In many organic compounds, by the action of chlorine, a certain number of equivalents of hydrogen are eliminated in the form of hydrochloric acid; the eliminated hydrogen being replaced by a like number of equivalents of chlorine, in such a manner that the chemical character and the fundamental properties of the original compound are not sensibly altered. The chlorine molecules, therefore, must take the place of the hydrogen molecules, and play in the new compound the same part which was performed by the hydrogen molecules in the original."

Although these views met with great opposition at first, many facts were subsequently discovered by Dumas and others which gave the strongest support to Laurent's views, but when Hofmann began his work *No organic base*, he tells us, *was known in which the hydrogen had been replaced by chlorine* in such a manner as not to materially change its properties. And yet, he adds, it would be an argument of the greatest weight, were chlorine, an electro-negative element, to be introduced into a compound possessing electro-positive properties without, however, changing its chemical character. Hence, he undertook his research, and naturally resorted to aniline.

He had already chlorinated aniline, and had obtained, along with much trichlorophenol, a very small quantity of a neutral substance which he only subsequently recognised as trichloraniline; and Fritzsche had prepared tribromaniline, with which he was well acquainted. But Hofmann was in no way misled by these observations—he recognises that—"In these cases the action has evidently gone too far for the aniline still to preserve its original character, and

it remained therefore to try in some way to regulate the action so as to produce compounds in which only one equivalent of hydrogen was replaced, and which, like aniline, might possibly possess basic properties." He therefore repeated his earlier experiments, and attempted to chlorinate aniline, but failed to obtain better results.

Failure to Hofmann, however, even at this early date as ever afterwards, was but the incentive to renewed efforts. At once it occurs to him to chlorinate anthranilic acid, in the expectation that—as this acid was known to yield aniline on distillation—the chlorinated acid would afford the desired chloraniline; and he further foresees the probability that nitrobenzene would yield a chlorinated derivative which would require only to be treated with sulphuretted hydrogen to be changed into the desired compound. But while engaged in preparing anthranilic acid, "another expedient offered itself," he tells us, "which by changing completely the direction of my researches led me quickly to the desired object." Remembering that it was not necessary to convert indigo into anthranilic acid in order to obtain aniline, but that this latter might be directly produced from it "*as a true product of oxidation*" by distillation with potash, he asks is it not in the highest degree probable, not to say certain, that isatin, a product of the oxidation of indigo, will be converted into indigo by fusion with potash; in which case the chlor- and dichlor-isatin already described by Erdmann may be expected to give chlor- and dichlor-aniline.* The experiment with isatin proving successful, mono- and dichlor-aniline were easily prepared.

It is impossible not to recognise that the train of argument thus made use of, at a time when so little was known of constitution as we now understand it, was eminently philosophical and comprehensive, and this is equally true of his treatment of his results. After fully describing a series of chlorinated and brominated anilines, he remarks that no two constructions can be placed on the facts he has discovered. They prove, in an undoubted manner, that in certain circumstances chlorine and bromine can perform the part of hydrogen in organic compounds. But he subsequently adds—

"It appears, however, that the chlorine preserves, to a certain extent, its electro-negative character, in those compounds in which it replaces hydrogen,

* It is clear that Hofmann's attention had at this time been very specially directed to previous researches on indigo, as a very lengthy abstract of the work of Dumas, Erdmann and Laurent, prepared by him, is published in *Liebig's Annalen* at the end of 1843 under the title "Uebersicht der in letzter Zeit unternommenen Forschungen über den Indigo und seine Metamorphosen." This abstract is wrongly included in the Royal Society's Catalogue of Scientific Papers among Hofmann's original contributions.

and that in proportion to the increase in the number of equivalents of the latter, for which chlorine or bromine are substituted, so is this character the more impressed on the resulting compounds. The compound atom aniline, $C_{12}H_7N$, in consequence of the peculiar arrangement of its elements, possesses the property of uniting with an acid ; replace one equivalent of its hydrogen by bromine and we obtain bromaniline, a body possessing likewise basic properties, but in a feebler degree, ... substitute now another equivalent of bromine for hydrogen, and we have dibromaniline. The facility with which all its salts are decomposed evidently indicates that the basic character of aniline is further enfeebled by the repeated assumption of bromine. Finally, in tribromaniline the electro-negative properties of the assumed bromine equivalents have placed themselves in equilibrium with the electro-positive character of the original system."

While confirming the truth of the principle put forward by Laurent, Hofmann therefore clearly recognised the limitations to which it must be subjected; and nothing has since been discovered which would lead us to state the substitution theory in terms other than those he adopted.

It is remarkable to what an extent Hofmann's activity now became manifest, and how rapidly he extended the field of his investigations. At Liebig's suggestion, Dr. Blyth and he undertook the investigation of fluid storax balsam (*Chem. Soc. Memoirs*, **2**, 334, April, 1845). At the same time, recognising the importance of bases, he set to work with Muspratt to apply Zinin's method of reducing nitro-compounds generally ; and commencing with nitro-toluene, they discover paratoluidine (*ibid.*, **2**, 367, April, 1845). At the close of the paper, they refer to the production of nitraniline from dinitrobenzene. The subsequent special memoir on this latter subject (*ibid.*, **3**, 111, March, 1846) opens with an elaborate discussion of the action of nitric acid on organic substances and of the nature of nitro-compounds; as we read this we realise how absolutely vague were the ideas which then existed on this subject. But Hofmann's perceptive power is again at once apparent, for the style is so essentially his that there can be no question that his views especially are being put forward. Laurent's diagnosis of the nitro-compounds is singled out as clearly in advance of all others, and the conclusion advocated that

"Many products which have assumed nitrogen and oxygen from nitric acid may indeed be regarded as simple products of substitution, in which the hydrogen instead of being replaced by chlorine or bromine, is replaced by a compound radicle, namely, by hyponitric acid (NO_4)."

As the displacement of hydrogen by hyponitric acid had been limited to acid and neutral substances, it appeared to be a point of great interest to ascertain whether, indeed, NO_4 could also displace hydrogen in basic compounds without destroying their electro-positive character.

Taking into account the various ways in which aniline was formed, its characteristic properties, and, above all, the fact that hydrogen could be displaced in it by bromine and chlorine, they deemed this substance the best suited to their experiments. Failing, however, in their attempt to nitrate it, and also to nitrate isatin, and foreseeing, also, that nitrosalicylamide—a substance prepared by Cahours a short time previously—could not be expected to yield nitraniline, as salicylamide gave but very little aniline on distillation, they asked themselves whether it might not be possible to partially reduce dinitrobenzene. In times when so little was established about the nature of nitro-compounds, such an argument cannot have been so self-evident as it now appears to be, even to the beginner; indeed the fixity of purpose—based, doubtless, on their clear theoretical conception of the nature of the problem they had in hand—displayed by Hofmann and Muspratt on this occasion, is specially noteworthy. Just as they were about to make the experiment, Zinin published a paper in which it was stated that dinitronaphthalene and dinitrobenzene were entirely deprived of their oxygen on reduction by sulphuretted hydrogen; and that, whereas it was to be expected that the former would yield a base corresponding to it in composition, $C_{20}H_{10}N_2$, to judge from the analysis of the platinichloride prepared from the base, its equivalent was only half as great, viz., $C_{10}H_8N$; Zinin, therefore, came to the conclusion that a division had taken place, and, consequently, gave the name seminaphthalidine to the product of reduction. This, it will be remembered, was in days before the importance of Avogadro's law had been impressed on chemists by Canizzaro, when the methods of rigidly determining molecular weights such as we now regularly use were in their first infancy. Zinin's researches—Hofmann and Muspratt tell us—appeared to cut off all hopes of their ever obtaining nitraniline; nevertheless they considered a continuation of their experiments in every way desirable, and soon obtained results which had escaped the observation of Zinin; these brought them to the point they aimed at. As every student of the elements of organic chemistry now knows, nothing is easier—following Hofmann and Muspratt—than to obtain nitraniline from dinitrobenzene; and, moreover, the method of partially reducing nitro-compounds thus introduced by them has proved of service in many other cases. Nitraniline was found to have the properties of an exceedingly weak base. Its production is spoken of as "interesting in reference to the question of substitution, which is still in debate among chemists. If we reject that theory—they remark—we can scarcely understand the constitution of this base and its relation to aniline."

But, as showing how limited was the knowledge of that time, it is noteworthy that the memoir concludes with a reference to the

compound obtained by Zinin from dinitrobenzene, in which it is pointed out that probably this is but a product of the further reduction of nitraniline in accordance with the equation

$$\underset{\text{Nitraniline.}}{C_{12}H_6N(NO_4)} + 6HS = \underset{\text{Semianiline.}}{2C_6H_4N} + 4HO + 6S.$$

Historical facts such as this serve to remind us how great has been the influence exercised by the systematic adoption of physical conceptions by chemists.

Although it was some time before the arguments of Berzelius and his school came to be regarded as futile, the results obtained by Hofmann in the course of his investigations of the chlor- and bromanilines and of nitraniline had—it is well known—considerable influence on the minds of chemists, and largely promoted the ultimate acceptance of the substitution theory.

* * * * *

A new chapter in Hofmann's work now begins to open; the first reference to this is at the close of his memoir on the metamorphoses of indigo, where we read—

"Before concluding this memoir, I shall mention another compound which appears worthy of the attention of chemists. It is formed by passing into aniline, free from water, a stream of cyanic acid. . . . It is a kind of urea in which the ammonia is displaced by aniline. I was in hopes that this body would possess basic properties, and, like urea, form crystalline salts with nitric and oxalic acid; its properties are, however, very different."

The theme is still further developed in a brief note on "New Researches on Aniline," communicated to the Chemical Society in December 1845 (*Memoirs*, 3, 26), the opening paragraph of which is as follows—

"In my former papers upon aniline, I had repeated opportunities of pointing out the remarkable analogy which exists between this body and ammonia, and at the conclusion of my memoirs on chloraniline and bromaniline, I announced the existence of a compound which may be considered as urea in which ammonia is replaced by aniline. The discovery of this substance opened a new field for research, inasmuch as it was to be expected that all the relations exhibited by ammonia, and the metamorphoses it undergoes, might be realised with aniline.'

This theme may be said to have occupied him during the rest of his scientific career, for the elaboration of the chemistry of the amine type soon became the work of his life.

The note last referred to admirably illustrates Hofmann's style, especially his remarkable quickness in perceiving and availing himself of opportunities, his powers of generalisation, and the manner in which, without the slightest loss of time, he proceeded to develop his attack in a variety of directions as soon as a new observation

was made and a new problem indicated. In a few lines we are told that the comportment of aniline with cyanic acid induced him to subject it also to the action of cyanogen and chloride of cyanogen; that sulphide of carbon readily acts on it, forming sulphocarbanilide that, inasmuch as the new substance from urea and cyanic acid might be considered as aniline which had lost one equivalent of hydrogen and assumed the elements of carbonic oxide—as *carbanilide* —it was probable that it might be produced by means of phosgenic gas, and the experiment being tried, such proved to be the case. Finally, reference is made to the action of oil of mustard, of trichloride of phosphorus, and of chloride of silicon on aniline as giving rise to crystalline products.

All these observations were subsequently elaborated, but it was not until several years later that most of them came to fruition. Some considerable time was spent in studying the action of cyanogen and of iodine from the point of view of the substitution theory, as the imperfect knowledge then at the disposal of chemists of the influence of these electro-negative radicles on organic substances seemed to indicate a marked difference between their action and the effects which chlorine and bromine, so analogous in every other respect, produced under the same circumstances.

Hofmann found (*J. Chem. Soc.*, May, 1848, **1**, 269) that iod-aniline may be obtained by the direct interaction of iodine and aniline, and that it was a weakly basic substance. He failed, however, to obtain any higher iodo-derivative, and pointed to the action of the three halogens on aniline as affording an interesting illustration of the decreasing affinity which chlorine, bromine and iodine manifest for hydrogen. It is of interest, historically, that reference is made in this paper to the ingenious process devised by M. Melsens for substituting hydrogen in the place of chlorine in acetic acid by means of a weak amalgam of potassium. Experiments on the process made with Dr. Kolbe when he was in London, are referred to, showing that chlor- and brom-aniline were reconverted into aniline with the greatest facility by its means. We are thus reminded that sodium amalgam was not yet recognised at this time as an all-powerful reducing agent.

* * * * *

The action of cyanogen on aniline was described before that of iodine (*ibid.*, April, 1848, 159). The product, which, perhaps unfortunately, was named *cyaniline*, proved to be composed of the elements of aniline plus those of cyanogen, not a substitution compound analogous to those obtained by the action of halogens. Toluidine and also cumidine—the base which Nicholson, one of Hofmann's pupils, had described but a short time previously—gave similar pro-

ducts; not only ammonia, but also nicotine and leucoline (quinoline), however, were found to behave altogether differently, and Hofmann takes the opportunity of pointing out that, although they resemble aniline in a great many respects, these two bases seem to belong to a perfectly different class of alkaloïds.

Cyaniline is spoken of as the first instance in which an organic alkali is found associated with another compound the presence of which does not affect its saturating capacity—it is regarded as a *conjugated base*, the counterpart of *conjugated acids*, such as formobenzoic and hippuric acids, a view which is practically identical with that now held.

Hofmann, in this memoir, gives utterance to important views on the constitution of the alkaloïds generally, whilst guarding himself from entering upon the often disputed question whether they were compounds of ammonia or amidogen—a question which was soon to receive its solution at his hands. The notions of a relation between the amount of nitrogen in organic bases and their saturating capacity, emanating from Liebig's earlier experiments on this subject, lost their significance—we are told—on the discovery of alkaloïds containing more than one equivalent of nitrogen . . . . Nevertheless, a relation between the nitrogen and the saturating capacity remained extremely probable, and chemists commenced to assume the nitrogen as existing in these bases in two forms. In almost all cases that portion of this element to which the basic properties were referred was believed to be in the form of amidogen, ammonia, or oxide of ammonium, whilst the views respecting the other portion were for the most part less decided. Hofmann then criticises views put forward by Fresenius, based on the composition of nitraniline, pointing out their arbitrary character, and that in a class of compounds so rich as that of the organic bases, a greater variety is to be expected than is admissible on the assumption that they resemble nitraniline. He is willing to admit that possibly some may contain an oxide of nitrogen, and that others may be cyanogen compounds, but adds, however, that a great many other modes of constitution may be imagined which present a similar degree of probability.

Failing to obtain a cyanogen substitution derivative of aniline by means of cyanogen, nothing was more natural than to attempt its preparation by means of chloride, bromide and iodide of cyanogen, and, consequently, we find the third paper of the series entitled "Researches on the Volatile Organic Bases" devoted to this subject (*J. Chem. Soc.*, June, 1848, **1**, 285); as indicating the gradual development of Hofmann's views on the constitution of the amines, this paper is full of interest.

It contains an account of *melaniline* (now known as diphenyl-

guanidine), a compound formed by the action of cyanogen chloride and bromide on aniline "produced by the fusion of two aniline atoms which have lost one equivalent of hydrogen in the form of hydrochloric acid, and have simultaneously assimilated a proportional amount of cyanogen." The name appears to have been chosen to indicate the supposed analogy of the substance with the melamine discovered by Liebig. Besides a description of melaniline and its salts, and of dichloro-, dibromo-, diiodo- and dinitro-melaniline, the memoir contains an account of the behaviour of melaniline with cyanogen, which is characterised as remarkable owing to the assimilation of two equivalents of cyanogen, both the aniline atoms (the intimate combination of which constitutes melaniline) exhibiting, it would seem, the same comportment with cyanogen as when in the isolated state.

Hofmann speaks of melaniline as a conjugated base of a similar, although more complicated, constitution than cyaniline. He points out that the capacity which we observe in aniline of combining with other substances without losing its basic properties, has by no means reached its limits in melaniline; in dicyanomelaniline we see two new equivalents of cyanogen enter into the compound, and some preliminary experiments appeared to indicate that this accumulation round the original atom may be carried still farther. "Facts like these," he adds, "deserve particular attention, containing as they do new confirmations of a general view of the organic bases which is daily gaining ground." At a very early period, he goes on to state, as far back as 1837, Berzelius, on the ground of Liebig's researches, expressed the opinion that the natural alkaloïds, which at that period engrossed the undivided attention of chemists, were peculiar ammonia compounds—conjugated compounds, in which the chemical character of ammonia, modified, indeed, by its conjunct, was still perceptible. This view, which was principally founded on the remarkable analogy of the ammonia salts with the salts of the alkaloïds, met by no means with general approbation when first stated; but it had been retained and carried out by Berzelius with the perseverance and ratiocination which are peculiar to that great chemist, and it could not be denied that since that period science had acquired a great number of facts which powerfully supported his opinion.

He then proceeds, in his clear manner, to dilate at length on these facts, and to interpret them in support of the view held by Berzelius. Finally, we come to the following remarkable passages:—

"All these considerations render it exceedingly probable that the organic bases are indeed conjugated ammonia compounds. It is true we are not able, at present, to isolate the ammonia without entirely destroying the compounds; and it is a question whether we shall ever find a method of

separating and reuniting the proximate constituents which the theory of Berzelius supposes in these alkaloïds, in the same manner as we effect the separation and reunion of acid and base in a salt. Vainly have I hoped in the course of my investigations of this subject to see aniline split up into ammonia and the conjunct

$$C_{12}H_4.$$

"Possibly this separation may succeed in the hands of a more happy experimenter; possibly it may ever remain unaccomplished; nevertheless, the adoption of Berzelius's theory will prove a great benefit, even if it were only to aid the memory and to facilitate the study.

"All our formulæ, our whole nomenclature, would be simplified by such an adoption. No longer should we have anilides, naphthalides, and cumidides; these substances becoming anilo-amides, naphthalido-amides, and cumido-amides; and by introducing conventional symbols for the conjuncts, every compound might be expressed rapidly and concisely.

"By considering the alkaloïds as conjugated compounds of ammonia, cyaniline, and melaniline become conjugated ammonia compounds of the second order, or, in other words, the original ammonia atom has become associated with the conjunct, $C_{12}H_4$ = An, and with other substances, and the rational formulæ of these compounds now assume the following shape—

Ammonia	NH_3.
Aniline	$NH_3(An)$.
Cyaniline	$NH_3(AnCy)$.
Melaniline	$NH_3(An_2AdCy)$.
Dicyanomelaniline	$NH_3(2AnCy,AdCy)$.

Such fervid advocacy of the Berzelian hypothesis is very remarkable when we recollect that his first experiments with aniline led him to conclude that it was *phenamide*, $C_{12}H_{10}{\cdot}N_2H_4$; and also that he was the pupil of Liebig, who held a view very different from that of Berzelius, in entire harmony with Hofmann's own early conception of the nature of the base. His attitude at this time towards the great question of the nature of the organic bases is truly striking testimony of the influence then exercised by the great Swede, especially as a few months later the force of facts caused him to return to his original faith; indeed, to place the truth of Liebig's view beyond all question.

The fourth of the researches on the volatile organic bases deals with the preparation and properties of anilourea (phenylcarbamide) from aniline and cyanic acid, of carbanilide (diphenylurea), and of sulphocarbanilide. It is an unusually tersely written, purely practical communication.

The next (*J. Chem. Soc.*, November, 1849, **2**, 300) is of special interest, and marks an entire change of front in Hofmann's views regarding the organic bases. It is divided into several sections, the first of which on the action of acids and bases on cyaniline needs no comment; the second, on metamorphoses of dicyanomelaniline

records, among other things, the discovery of carbanil (phenyl isocyanate), now an analytical agent of great value in determining the presence of alcoholic hydroxyl.

The gradual evolution of ideas noticeable in this memoir is very striking. The product obtained on subjecting dicyanomelaniline to the action of concentrated hydrochloric acid is a yellowish, indistinctly crystalline substance, $C_{30}H_{11}N_3O_4$. Having in mind the fact that cyaniline was converted under similar circumstances into oxalates of aniline and ammonia, or rather into compounds derived from those salts by elimination of water, Hofmann's insight at once led him to regard the yellow substance as melaniline binoxalate less four equivalents of water, and he shows that it yields melaniline and oxalic acid when subjected to the action of alkali. He then points out that it belongs to a daily increasing class of compounds derived from acid salts of ammonia, or of organic bases, by elimination of four equivalents of water, such as succinimide, and he therefore terms it *melanoximide*, a name which is not inappropriate even from our modern point of view.

$HN{:}C\begin{cases}NHPh\\NHPh\end{cases}$	$HN{:}C\begin{cases}NPh{\cdot}C{:}NH\\NPh{\cdot}C{:}NH\end{cases}$	$HN{:}C\begin{cases}NPh{\cdot}CO\\NPh{\cdot}CO\end{cases}$
Melaniline.	Dicyanomelaniline.	Melanoximide.

He attempts to prepare melanoximide from binoxalate of melaniline, but fails owing to the facility with which melaniline itself decomposes when heated. In carrying out these experiments, however, a "peculiar, somewhat cyanic odour," which had frequently been noticed during the investigation, was developed to an unusual extent, and "I began to hope," says Hofmann, "that I should at last succeed in securing this enigmatical body which I had vainly chased on so many occasions." But he did not succeed until he began to study the action of heat on melanoximide itself. On subjecting this compound to dry distillation, much gas—chiefly carbonic oxide—was disengaged, a yellowish liquid distilling over "of a most powerful odour, recalling at once the odour of aniline, of cyanogen, and hydrocyanic acid, provoking lachrymation in a most fearful manner, and exciting, too, in the throat the suffocating sensation produced by the latter." The quantity of crude liquid obtained amounted to about 10 per cent. of the melanoximide used, and this only when water was carefully excluded, which readily decomposed the liquid. The formula of the new substance is ascertained to be $C_{14}H_5NO_2$, and subtracting from this the elementary difference distinguishing aniline from ammonia, $C_{12}H_4$, the formula of hydrated cyanic acid, C_2HNO_2 is arrived at; the name *anilocyanic acid* is therefore assigned to it. Subsequently he pointed out that as it may also be regarded

as bicarbonate of aniline minus four equivalents of water, the name anilo-carbimid, or in Gerhardt and Laurent's nomenclature the term *carbanite* might be used for the new product.

The chemistry of this remarkable substance is forthwith fully developed, its behaviour being shown to be in all respects similar to that of cyanic acid towards acids, bases and alcohols, attention being specially directed to the formation from it of compounds corresponding to the urethanes previously obtained by Liebig and Wöhler from cyanic acid and alcohols.

Hofmann here gives utterance to the pathetic lament that

"Unable to indulge in a more detailed study of these beautiful reactions in consequence of want of material, I must postpone their completion until a simpler method may have been discovered of obtaining in a shorter time a larger quantity of anilocyanic acid."

He then speaks of the long and complicated series of metamorphoses involved in the preparation of the substance, commencing with that of aniline from indigo or benzole, having caused no small expenditure of time and labour, and recognising how much he was indebted to others, he adds

"Nor could I have found sufficient leisure to follow out the manifold ramifications of the aniline family in its numerous and so often intricately related derivatives . . , had it not been for the valuable assistance and co-operation of Messrs. Nicholson and Abel, assistants in the College of Chemistry."

After further discussing the action of heat on melaniline and melanoximide, Hofmann draws attention to the recent experiments of Wurtz on the compounds of the alcohol radicles with cyanic acid (the cyanic ethers), pointing out that in these substances, as in anilocyanic acid, the original habits of cyanic acid in its behaviour with other bodies are retained in almost every direction, and he therefore groups anilocyanic acid along with them as cyanate of phenyl.* He finds, however, on pursuing the analogy to a practical end that cyanate of phenyl is not produced under circumstances which give rise to the formation of cyanate of methyl—by distilling a mixture of a sulphophenate with cyanate of potash, for example. He also fails in obtaining cyanide of phenyl by distilling cyanide of potassium with a sulphophenate, and is in consequence led to remark on the different behaviour of phenyl alcohol and ordinary alcohols.

Throughout this investigation, Hofmann's attention had been specially directed to the effects produced by the withdrawal of water from the salts of organic bases; and this subject naturally next claims his attention. He arranges the various derivatives of aniline

* It is here apparently that the term *phenylamine* is first used.

formed by the withdrawal of water from aniline salts in a table in comparison with the corresponding ammonia derivatives, and calls attention to the entire absence of anilonitriles or compounds derived from a neutral aniline salt by the elimination of four equivalents of water in the same way that cyanogen is formed from oxalate of ammonia. Experiments are then described which he had made with the object of filling up the blank, but without success. At once the question follows—

"What then, may we ask, is the reason why aniline, which so faithfully imitates the habits of ammonia, refuses to follow its example with respect to the formation of the nitriles? The answer to this question involves a careful consideration of the constitution of aniline and of the analogous bases."

Reference is then made to the paper before dealt with in which a synopsis was given of the facts supporting the view of Berzelius that the organic bases are conjugated ammonia compounds, in which ammonia pre-exists. According to this view, oxalate of aniline is represented by the formula $H_3N\cdot(C_{12}H_4)HC_2O_4$. But this formula gives no satisfactory answer to the above question. There is no comprehensible reason, Hofmann points out, why the oxalate of ammonia in the aniline salt should not be deprived of its four equivalents of water, and why the residuary cyanogen should not be associated with the usual adjunct.

According to Liebig, however, the organic bases have to be considered as amidogen compounds, and on regarding aniline as an amidogen compound the question appears in a perfectly different light. It is easy to see that the elimination of four equivalents of water from the neutral salt, $(C_{12}H_5)H_2N\cdot HC_2O_4$, is altogether impossible without the destruction of the term $C_{12}H_5$ (phenyl). Then comes the following modest reference to the great discovery which must ever rank highest among Hofmann's achievements, as it once for all settled the question that had so long been under discussion, and which was of such immense consequence to the chemistry of the amines and therefore of nitrogen.

"It is probable that considerations like those developed in the preceding pages will naturally assist in the elaboration of more rational views respecting the constitution of the organic bases. The apparent impossibility of obtaining an anilocyanogen throws some doubt on the pre-existence of ammonia in aniline. It is probably more in conformity with truth to consider aniline as a substitution product, as ammonia in which part of the hydrogen is replaced by phenyl (he does not appear to remember that he himself took this view originally); and this opinion may, perhaps, meet with the approbation of the Society, if I mention that a series of researches on the action of the bromides of the alcohol radicles on aniline and on ammonia have enabled me actually to replace

the basic hydrogen of these substances, equivalent for equivalent, by the alcohol radicles, and to produce in this manner a numerous series of new alkaloïds which appear to admit of no other mode of interpretation."

* * * * *

We have now to pass to the consideration of Hofmann's "Researches regarding the Molecular Constitution of the Volatile Organic Bases," the first of which was read to the Royal Society on January 17, 1850, having been received on December 26, 1849; it was printed in the *Phil. Trans.*, 1850, **1**, 93 (*J. Chem. Soc.*, **3**, 279), and was his first communication to the Society.

At the outset, he refers to the two theories of chief importance which had been enunciated respecting the constitution of the organic bases—those of Berzelius and Liebig; after remarking that the former had, in course of time, become more and more generally accepted—by himself among others, as we have seen—he draws attention to his own recent discussion of the question, and to his having shown that the analogy which had been so generally recognised as obtaining between the salts of ammonia and of the organic bases broke down just at the point where its occurrence would have been most decisive, thus greatly neutralising the force of the argument in favour of the ammonia theory; whilst, on the other hand, this very failure was not only in perfect harmony with, but would be required by, the theory of amidogen bases.

He then proceeds to speak of the recent discovery of methylamine and ethylamine by Wurtz in very remarkable terms, which are deserving of attention at the present time, when it may not be too late to recover fuller information as to the exact manner in which Hofmann was influenced by the work; and in order, also, that the precise relationship of the researches of two such distinguished investigators may be made clear, as well as their relative effect in forming opinion at the time.

Hofmann's eloquent words seem to admit of little doubt as to their meaning, and yet it is a question whether they do not convey a false impression. He says:—

"Yet stronger grounds for the acceptance of the latter view—the amidogen theory—have been afforded by a splendid investigation of M. Wurtz on the compounds of ethers with cyanic acid, which have actually realised a series of substances, anticipated in a most remarkable manner by Liebig on the theoretical ground of his conception of the nature of these compounds. Instances of such anticipation of discovery are so rare that I may be allowed to quote the words in which Liebig predicted, nearly ten years ago, the discovery of M. Wurtz:—'If,' said Liebig, in continuing the development of his ideas respecting the constitution of the organic bases, 'we were able to replace by amidogen the oxygen in the oxides of methyl and ethyl, in the oxides of two basic radicles, we should without the slightest doubt obtain a series of compounds

exhibiting a deportment similar in every respect to that of ammonia. Expressed in symbols, a compound of the formula $C_4H_5 \cdot H_2N = E \cdot Ad$, would be endowed with basic properties.' Now these compounds, imagined in 1840 by Liebig, in illustration of his views, have sprung into existence in 1849 with all the properties assigned to them by that chemist. At the beginning of the present year, M. Wurtz, in investigating the cyanates of ethyl, methyl, and amyl, arrived at the unexpected result that these compounds, when decomposed by potassa, undergo a change analogous to that of cyanic acid. This acid, when treated with potassa, yielding carbonic acid and ammonia, the corresponding ethers were split into carbonic acid and compound ammonias of the exact formula indicated in Liebig's suggestion. It would be difficult to imagine any more brilliant triumph for any theoretical speculation."

If we turn to Hofmann's obituary notice of Wurtz (*Ber.*, 1887, c, 815—996), one of the most brilliant and interesting of the many marvellous biographical sketches of his contemporaries for which chemists will ever be most deeply indebted to him, we find little to help us, and certainly no justification of the statement above quoted *implying* that the discovery of the amines by Wurtz was at the time regarded as affording special grounds for the acceptance of the amidogen theory.

That it excited extraordinary attention there can be no doubt. Hofmann, indeed, tells us that in the whole course of his experience no piece of work ever produced such an impression on the chemical world. Of this we have independent testimony in the fact that Wurtz's papers are reproduced in *Liebig's Annalen* with an editorial postscript, in which it is pointed out that whereas it has been the practice to await the appearance of complete publications before noticing them in the *Annalen*, an exception is made on behalf of Dr. Wurtz's important investigations. Not only are his papers reproduced from the *Comptes rendus*, but also Dumas' report to the Academy, to which a note by Liebig is appended.

If we refer to Wurtz's own statements, we find that, in his brief paper on ethylamine and methylamine (*Compt. rend.*, Feb., 1849, **28**, 223), after pointing out that the ammonia compounds, in a measure, come between the inorganic and organic compounds, he remarks that ammonia would be regarded as the simplest and strongest organic base—that it would be considered by all chemists as the type of this numerous class, if it were not separated therefrom by an undoubtedly important characteristic, to which, however, perhaps too much importance had been attached. It contained no carbon. But it appeared that this difference in composition was not sufficient to separate ammonia from the organic bases. He had succeeded in preparing a true organic compound from this alkali by adding the elements either of the hydrocarbon C_2H_2 or C_4H_4, without depriving it of its character

as a strong base, or even of its most characteristic property—its odour.*

Wurtz clearly regards his discovery as that of *organic* or *compound ammonias*. This is also the view taken by Dumas in his report on the paper; and it is easy to understand that a substance having the properties of aniline, although basic, should have failed to take rank directly with ammonia—consequently, that the discovery of substances *so exactly like ammonia* as are methylamine and ethylamine should have produced a profound effect.

Wurtz, it is true, points out that the compounds he describes may be regarded as methyl and ordinary ether respectively in which one equivalent of oxygen is displaced by one equivalent of amide, NH_2; or as ammonia in which one equivalent of hydrogen is displaced by methyl or ethyl—as methyl- and ethyl-amide;† but he does nothing more. Whilst Dumas, in his report, represents the new alkaloïds, and a number of others with which he compares them, as conjugated ammonias.

Liebig, indeed, in his editorial note, draws attention to this, and proceeds to recapitulate what he had written 12 years previously in advocacy of the view that the organic bases were amidogen compounds.

It would, therefore, seem that it is justifiable to claim for Hofmann the sole credit for the establishment of the *constitution* of the amines.

The argument which led Hofmann to institute his experiments is stated in the following passage—

"If we give to Liebig's view the extension of which it naturally admits,

* In his obituary notice of Wurtz (p. 932), Hofmann makes an interesting statement with regard to the discovery of ethylamine, which apparently is not to be met with in Wurtz's papers. He points out that it is easy, on reading the account given by Wurtz, to underrate the difficulties he encountered in interpreting his results, and that in fact the cyanic ethers had been some considerable time in his hands before he recognised the nature of the change they underwent when acted on by alkalis. Chemists were then under the influence of the recent discovery by Kolbe and Frankland of the formation of ammonia and an acid of the acetic series from the alcoholic cyanides, and it seemed not improbable therefore that a cyanate would give ammonia and an oxygenated acid. Wurtz actually found that on heating ethylic cyanate with alkali, an alkaline gas was evolved, which he for some time regarded as ammonia, but the solution contained only carbonate. For some time he sought in vain, Hofmann tells us, for a compound containing the complementary carbon of the cyanate; at last, one day the alkaline gas took fire and burnt with a luminous flame—like so many other important discoveries, that of ethylamine therefore was partly attributable to accident.

† Later in the paper—and always subsequently—he uses the names methyl*amine* and ethylamine—qui ont la même termination que ceux des autres alcalis organiques.

and which is demanded by the onward steps of science, we arrive at a more general conception of the nature of the organic bases; amidogen and the amides now presenting themselves to us only as particular instances of the permutations possible among the elements of the primary type ammonia. It seemed but logical to look among the bases for analogues, too, of the imidogen compounds and the nitriles. In other words, it appeared desirable to inquire whether the several equivalents of hydrogen in ammonia could not be replaced, not only by atoms neutralising the basic properties of the original system, but also by elements or groups of elements, not affecting or but slightly modifying the alkaline character of the primary compound. Were this possible, we should arrive at the formation of three classes of organic bases, derived from ammonia by the replacement respectively of one, two, or three equivalents of hydrogen."

He then goes on to say—

"In commencing my experimental inquiry, the first step was to select the particular base which should be the subject of operation, and the radicles whose introduction should be attempted. On the one hand, my previous occupations suggested aniline for the foundation; while, on the other hand, the radicles existing in aniline and its congeners, methylamine, ethylamine, and amylamine, namely phenyl, methyl, ethyl, and amyl, presented themselves as materials for construction."

From this passage it is clear that the investigation was carried out with full knowledge of the discovery made by Wurtz, which is evidence that Hofmann himself at the time did not regard the production of organic ammonias from cyanic ethers as proof of their constitution.

At first the attempt was made to introduce a second equivalent of phenyl into aniline by means of phenol, by heating the two substances together at a high temperature, but unsuccessfully. The action of chloride and bromide of phenyl upon aniline promised a better result, but the difficulties encountered in preparing these compounds deterred him we learn from further pursuing this direction of the inquiry. He was entirely successful, however, in substituting methyl, ethyl and amyl for the remainder of the basic hydrogen in aniline, using for the purpose the bromides or iodides of the radicles.

Self evident as the conversion of an amine by means of an alkylic bromide or iodide is to us, the issue of such an experiment must have been entirely problematical in 1849, when there were no precedents to rely upon. It is, therefore, to be regretted that no clear indication is given by Hofmann of his reasons for selecting the methods he used, and yet there can be little doubt that the remarkable use which Frankland but a short time before had made of the iodides of methyl and ethyl* had drawn the attention of

* In effecting the isolation of the organic radicles, and in preparing organometallic compounds (*J. Chem. Soc.*, June—November, 1849, 2, 263, 297). Frank-

chemists to the value of these compounds as agents, and that the use which Hofmann in turn made of them is traceable to this circumstance; all he tells us, however, is that "the compounds of these radicles (methyl, ethyl, &c.) with chlorine, bromine and iodine appeared to be the most appropriate substances" for the purpose he had in view. Their introduction as substituting agents, however, clearly dates from this time, as indeed, Hofmann himelf pointed out a few years afterwards—

"These successive substitutions (of hydrogen in ammonia) were accomplished by the action of ammonia upon the bromides of the alcohol radicles, which since that time have become most valuable agents of substitution in the hands of chemists" (*Proc. Roy. Soc.*, 1858, **9**, 151).

Aniline was without difficulty converted into ethyl- and diethyl-aniline, beyond which stage the substitution could not be carried.* As the passage of ammonia into aniline had been accomplished, as already pointed out, in the course of the experiments Laurent and he had previously made, in which phenol was acted on by ammonia at a high temperature—

"The formation of aniline, ethylaniline, and diethylaniline appeared to have established in a sufficiently satisfactory manner the point of theory in question."

Such are the words in which Hofmann recognises the bearing of his results: the calmness and apparent indifference with which he views his success is almost aggravating.

A true man of action, he at once goes on to remark—

"Still I thought desirable the acquisition of additional facts in support of the position to which this inquiry has conducted me. Thus I have been led to study the action of bromide of ethyl upon several of the derivatives of aniline, and to try whether other alcohol radicles, such as methyl and amyl, would have a similar action; lastly, in order to complete the investigation, I was obliged to leave the amidogen bases altogether, in order to submit the typical ammonia itself to examination."†

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land, in the introductory remarks prefacing the first of these papers in his volume of *Experimental Researches* (p. 65), in fact states: "In these experiments the iodides of the alcohol radicles were employed as reagents, I believe for the first time." As we know that, when Frankland's paper was communicated to the Society, "Dr. Hofmann exhibited a specimen of the zinc methyl he had obtained from Dr. Frankland, and demonstrated its spontaneous inflammability," it is evident that his attention had been very specially directed to the work. See also Frankland (*J. Chem. Soc.*, **3**, 48).

* It was afterwards recognised that the products obtained on this occasion were not pure substances. The preparation of pure methylaniline and the relative proportions of methyl- and dimethyl-aniline formed on methylating aniline by means of methyl chloride, bromide and iodide were fully gone into by Hofmann many years later (*Ber.*, 1874, 523; 1877, 591).

† The action of ethyl chloride on an alcoholic solution of ammonia was examined

The action of ethyl bromide on chlor- and bromaniline and nitraniline was first studied; the results obtained were important as throwing light on the constitution of these substitution bases. To quote Hofmann's words—

"The possibility of introducing into these substances* two equivalents of ethyl, shows that they must contain the same amount of basic hydrogen (an expression by which I may be allowed to represent briefly the hydrogen of the ammonia-skeleton) as aniline itself, and hence it is evident that it was the hydrogen of the phenyl which was replaced by chlorine, bromine, and hyponitric acid in the transformation of aniline into its chlorinated, brominated, &c., relatives. The transformation is due to a secondary substitution, affecting the hydrogen in the radicle which replaced the original ammonia-hydrogen."

This seems to have been the only occasion on which the hydrocarbon radicle in aniline in any way engaged Hofmann's attention or excited his curiosity—his interest in aniline seems to have been centred so entirely on its basic properties, his interest in bases to have been so great, that it was long before other problems in any way attracted him.

After preparing a variety of substituted amines from aniline, and showing that it was possible to displace the three hydrogen atoms in ammonia by three different hydrocarbon radicles, Hofmann showed that ammonia could be directly converted, not only into the ethylamine already prepared by Wurtz, but also into a di- and a triethyl derivative; and at once foreseeing the probability "that arsenietted and phosphoretted hydrogen, which imitate to a certain extent the habits of ammonia," would afford similar derivatives, he announces his intention of extending his researches to these hydrides, a promise which was amply fulfilled in after years.

Hofmann, in the first instance, speaks of the three kinds of base derived from ammonia as *amidogen*, *imidogen* and *nitrile* bases respectively. The terms primary, secondary and tertiary, to which we are so accustomed, appear to have been first used in a lecture which he delivered to the Chemical Society in June, 1858 (*J. Chem. Soc.*, **11**, 255), in which the classification of the various derivatives of ammonia—both amines and amides—then known is discussed at great length, reference being also made to the basic derivatives of phosphorus, arsenic and antimony. The closing words of this lecture are worth quoting—

in Hofmann's laboratory by C. E. Groves in 1861 (*J. Chem. Soc.*, **13**, 331). He obtained the monethylated compound almost exclusively. Hofmann, working on a large scale, subsequently obtained a mixture of mono-, di-, and tri-ethylamine containing a slight excess of the secondary amine (*Ber.*, **3**, 776).

* The statement here made that nitraniline could be methylated and ethylated was corrected in a later paper (*Roy. Soc. Proc.*, 1862, **12**, 639).

"In the preceding paragraphs I have endeavoured to give an outline of the chemical history of the type ammonia, such as it exhibits itself at the present moment. No department of chemistry, perhaps, reflects in a more salient manner the rapid progress of science during the last quarter of a century. Nearly all the bodies mentioned in this paper were discovered during that period; nine-tenths, in fact, the very compounds which have most assisted in the elaboration of our theoretical views, are the fruits of the last 10 years. Though much has been achieved, more is left to be done. But even now, while so many known substances remain to be finally grouped and classified, and while countless groups and classes remain to be discovered, yet the general features of the system are distinctly perceptible, and the time is rapidly approaching when, losing sight of the chaotic mass of overwhelming detail, the eye may rest with complacency upon the simple beauty of the law which governs the construction of the bodies belonging to the type of ammonia."

When we recollect how entirely we owe to Hofmann the establishment of the "simple beauty of the law" governing the constitution of amines generally, this passage may justly be selected as a fit epitaph to attach to his work.

The monamines were largely used by him in subsequent investigations, as will appear in the sequel, and therefore, in concluding the account of his researches of the monamines, it will only be necessary to refer here to the process which he devised of separating the ethylamines, and also to his proposals for effecting the diagnosis of amines.

Although they differ considerably in boiling point, it is impossible to separate the ethylamines by fractional distillation.* The "simple and elegant process," as he himself originally termed it, devised by Hofmann (*Proc. Roy. Soc.*, Nov., 1860, xi, 66) is based on the observation that when submitted to the action of ethylic oxalate, ethylamine is converted into diethyloxamide, a crystalline substance, only sparingly soluble in water; whilst diethylamine yields ethylic ethyloxamate, a liquid boiling at a high temperature; triethylamine remaining unchanged. Hence, after subjecting the mixture to the action of the oxalate, it is possible to separate the tertiary base by distillation, and to mechanically separate the crystalline amide from the oily oxamate; the amide may then be purified by recrystallisation from boiling water, and distilled with alkali, the oxamate being similarly treated after separating the dissolved oxamide by cooling to 0°, and then fractionally distilling the liquid.

* The boiling points, &c., of the various methyl- and ethyl-amines were determined by Hofmann in 1889 (*Ber.*, 699), with the aid of large quantities of purified material placed at his disposal by Kahlbaum. In describing his results he states that the experience gained in working on the large scale had proved that these amines were best prepared by his original method.

It was subsequently pointed out (*ibid.*, p. 526) that a simpler and more perfect separation of the oxamide and oxamate might be effected by submitting the mixture at once to the action of boiling water, when diethyloxamide dissolves, the oxamate remaining as an insoluble layer floating upon the hot solution. Hofmann re-examined the process ten years later, when the opportunity occurred to prepare the ethylamines on a large scale with the aid of ethyl chloride obtained as a bye-product in the preparation of chloral (*Ber.*, 3, 109, 776). The criticisms to which the method had been subjected were considered, and a full account was given of the manner of operating which experience had shown to be the best.

Provided that sufficient material be at disposal, the diagnosis of the amines is easily effected, following the indications afforded by Hofmann's inquiry, by ascertaining the number of methyl or ethyl groups which can be introduced in place of hydrogen, but the method involves the analysis of the product. A qualitative method of perfectly general application in the case of primary, but of restricted application in the case of secondary amines, was proposed by him in 1870 (*Ber.*, 3, 767), after he had discovered the isonitriles.

All primary amines yield the corresponding isonitrile when warmed with alcoholic potash and chloroform, and these nitriles are all possessed of intolerable odours. On the other hand, both primary and secondary paraffinoid amines form thiocarbamates with carbon bisulphide, and these are converted by mercuric chloride into mustard oils, which are also characterised by their evil odours.

By reversing the test, the primary amines become remarkably delicate tests of chloroform; it is possible, for example, to detect with certainty 1 part of chloroform in 5000 to 6000 parts of alcohol by means of aniline.

* * * * *

In the second memoir, entitled "Researches into the Molecular Constitution of the Organic Bases," published in the *Phil. Trans.* of the Royal Society (1851, ii, 357; Abstr., *J. Chem. Soc.*), Hofmann considers "the history of a new group of alkaloïds, which, although intimately connected (with the amines) by their origin, differ from them altogether by their properties, and especially in *not being* volatile." After having succeeded, he tells us, in replacing, step by step, one, two, or three equivalents of hydrogen in ammonia by a corresponding number of compound atoms, the question arose whether the agent by which these changes were effected would exert a still further influence on the last product of the action. In order to decide this question by experiment, he submitted two nitrile bases, diethylaniline and triethylamine, to the prolonged action of bromide of ethyl. These experiments did not lead to perfectly decisive results. It was evident

that in these cases an action ensued. . . . No doubt, however, could be entertained as to this action being altogether different from the preceding stages of the process.

A mixture of an aqueous solution of triethylamine and bromide of ethyl, sealed up in a tube, solidified after several hours ebullition, the crystals consisting chiefly of the fibrous hydrobromide of triethylamine, with which, however, a certain quantity of white, opaque, granular crystals was invariably mixed. Anhydrous materials were therefore used, in the hope of increasing the quantity of this latter substance, but the progress of the action was found to be retarded in a most remarkable manner by this variation, days elapsing before the conversion was completed. But the difficulty thus met with was soon overcome by using iodide instead of bromide of ethyl, action taking place almost instantaneously on warming a mixture of the anhydrous substances, the product—as every chemical tyro now knows—being an iodide formed by the direct combination of the triethylamine with the ethyl iodide.

The properties of the iodide thus produced are so remarkable, there is still so much that requires explanation in connection with such compounds, that the account Hofmann originally gave may be quoted almost verbally with advantage, both because it is historically full of interest, and in order that attention may be directed to a subject which is rarely more than superficially noticed in our text-books. It is in no way surprising that he should remark—

"I confess I had not anticipated the possibility of the existence of (such) a compound; it appeared at the first glance in direct opposition to the theoretical view repeatedly referred to. For if it was possible to decompose the new iodide by potassa, just as the preceding iodides, . . . if it was possible to separate from this substance a new volatile base analogous to the preceding ethylated alkaloïds, there was no reason why the process of ethylation should cease with the fourth equivalent of ethyl. On the contrary, it then appeared more than probable that the formations of ethylamine, diethylamine, and triethylamine, far from being due to the successive replacement of the various equivalents of hydrogen in ammonia, were rather to be considered as special instances of a far more general tendency of carbon and hydrogen to accumulate in organic substances.

"The eagerness with which I submitted this question to the test of experiment may be readily imagined"—Indeed, it may!—"On adding potassa to a solution of the iodine compound in water, the liquid solidified at once into a crystalline mass, which I took of course for the base existing in the iodide; analysis, however, soon showed that the substance thus precipitated is nothing but the iodide itself, which is less soluble in an alkaline solution than in pure water. The iodide was now distilled with a very concentrated solution of potassa for several hours; but during this time nothing but pure water passed over. The solution in the retort solidified on cooling to crystals of the unchanged iodide. When the solution of the iodide in

potassa had become very concentrated, it separated into two layers, an aqueous one and an oily one, which floated on the surface. But even now no decomposition had been induced, the oily stratum solidifying on cooling into a crystalline cake of iodide perfectly unaltered. It was only when the liquid was evaporated to dryness that a change took place; but then the change was no longer due to the action of the potassa, but to the influence of heat, and in no way differed from the decomposition which the crystals undergo when heated alone" (into triethylamine and ethyl iodide).

"The deportment with potassa of the new iodine compound altogether precludes the idea of considering it as an analogue of the hydriodides of ethylamine, diethylamine, and triethylamine, all of which are readily decomposed under the influence of the alkalis.

"However, the iodine, though it cannot be eliminated from the crystals by the alkalis, may be separated with the greatest facility by silver salts; in fact, the nitrate, the sulphate, the oxide of silver behave with the iodine compound exactly as with iodide of potassium or sodium. . . . In fact, the molecular group combined with iodine, in the compound under examination, behaves like sodium or potassium; it is a true organic metal in all its bearings. For this metal, I propose, on the ground of its formation and composition, the name tetrethylammonium (τέτρα), which implies that it is built up by the intimate union of nitrogen with four equivalents of the hypothetical hydrocarbon called ethyl, and that it may be viewed as ammonium, in which the whole of the hydrogen is replaced by an equivalent proportion of the above hydrocarbon."

"The new crystalline compound, according to this mode of viewing it, must be considered as iodide of tetrethylammonium, and its formation takes place in consequence of a transposition of the elements, which is perfectly analogous to that assumed by the followers of the ammonium theory in the formation of iodide of ammonium from ammonia and hydriodic acid."

We have here a complete statement of the ammonium theory of the constitution of such iodides and of analogous compounds, accepted in its entirety from the time of Hofmann's experiments up to the present day. But it is important to note that he explicitly guarded himself when putting this view forward by stating—

"I will not enter here into the merits of the ammonium theory; the question whether this mode of representing the constitution of the ammonia salts be correct or not may be left out of consideration for the present. The view I have taken of the new compound, and which I readily admit must stand and fall with the ammonium theory, has the great advantage of closely assimilating these substances to the compounds of mineral chemistry, whereby the nomenclature is essentially facilitated."

In the memoir under consideration there is much else that is of importance from many points of view. The iodide having been described, a full account is given of the remarkable properties of the hydrate formed on digesting it with silver oxide; and the extraordinary resemblance which this compound bears to the fixed caustic

alkalis is established in the most thorough manner possible. Among the properties of this substance to which reference is made, one deserves mention as somewhat singular, namely, the formation of a crystalline precipitate of the corresponding iodide on adding a concentrated solution of the tetrethylammonium hydrate to an alkaline solution of iodide of potassium. This phenomenon, it is pointed out, is due to the insolubility of the iodide in alkaline solutions, and not to the new base possessing a greater affinity for iodine than potassium. Another illustration of the readiness with which the iodide is formed is afforded by its production on boiling the hydrate (a concentrated solution) with ethyl iodide, the latter being converted into alcohol.

The memoir also contains a description of a number of mixed ammonium compounds analogous to the tetrethylammonium derivatives, prepared, for example, by combining methyl or amyl iodides with triethylamine, or from other nitrile bases than this last, as well as of the tetramethyl and tetramyl compounds. These were all found to exhibit the closest resemblance in their properties.

The behaviour of the hydrates is deserving of special mention. When a solution of tetrethylammonium hydrate ($NEt_4 \cdot OH$) is concentrated *in vacuo*, crystals are obtained of a hydrated compound. On evaporating such a solution on the water bath, decomposition sets in even before the water is completely driven off, the hydrate being resolved into triethylamine, ethylene and water, thus affording a means of preparing pure triethylamine. Hofmann also examined the behaviour of the amyltriethyl-, of the methyldiethylamyl-, and of the phenyltriethyl-ammonium hydrates, and in each case found that ethylene was the gas evolved. That the amyltriethyl compound should undergo decomposition in this way is somewhat remarkable, especially as the tetramyl derivative is resolved into triamylamine, water and amylene, and it is therefore noteworthy that the amyl compound is stated to be far less easily decomposed than the corresponding tetrethylammonium hydrate. Naturally, the tetramethylated compound was investigated, in the hope that it would afford methylene, but no gas was obtained from it; the precise nature of the change which it underwent was not determined.

Hofmann makes an important use of these facts, and of the properties of the substituted ammonium compounds generally, in discussing the constitution of the ammonia salts. The arguments he advanced nearly fifty years ago are still adopted at the present day, and, notwithstanding the attention since devoted to the subject, the problem remains much in the condition in which it was left by him—it will probably not be going too far to say entirely unsettled, conclusive in its favour though the arguments appear to be; nor is this strange, as

the settlement of the most difficult problem in chemistry is involved in its solution.

Several passages from this part of Hofmann's memoir merit reproduction here, if only as a model of lucid and philosophical statement.

"Without reproducing all the arguments brought forward by the supporters of the various theories (regarding the constitution of the ammonia salts), we may remember (he says) that, irrespectively of the impossibility of isolating ammonium itself, the instability of its oxide has been adduced as one of the most important objections against the assumption of the ammonium theory as originally suggested by *Ampère*, and subsequently elaborated by *Berzelius*. It deserves to be noticed that Berzelius expressly states that he considers the solution of ammonia gas in water as a solution of the hydrated oxide of ammonium. This idea, which is but a logical conclusion from the generalisation of the facts, is discountenanced to a certain extent by the chemical and physical character of this solution. Everybody knows that, even at the common temperature this liquid splits again into water and ammonia, while it still exhibits the character of the latter in so marked a manner as almost to preclude the idea that it had undergone as essential a change as the transformation into oxide of ammonium necessarily must be. Under these circumstances, some interest is attached to the discovery of a series of compound bases, corresponding in their composition to hydrated oxide of ammonium, from which they differ only by containing methyl, &c., in the place of hydrogen, and exhibiting a deportment which agrees much better with the anticipated character of such compounds as suggested by analogy. Here we find a very marked difference between the properties of the compound ammonia, and those of the ammonium oxide belonging to it; in the latter, we observe no longer any feature which could possibly betray the presence of the former; all their habits, volatility, odour, taste, &c., are totally changed; there is a difference between the two groups which is not inferior to that between ammonia and potassa. The solutions of the two oxides may be boiled for hours without the slightest quantity of the corresponding ammonia being disengaged; several of these oxides, containing more or less water of constitution or crystallisation, may actually be obtained in the dry state. It is evident that the arguments mentioned above, as adduced in refutation of the ammonium theory, cannot well be raised against the compound ammoniums. But who could deny the parallelism of these substances with the Berzelian type—with the oxide of ammonium?

"Again, many have found it difficult to conceive, that in the combination of ammonia with hydrochloric or hydrobromic acid, the hydrogen of the latter should leave the chlorine and bromine, for which it is known to possess so powerful an affinity, in order to unite with ammonia, converting it into ammonium. And they were the less inclined to admit of such a disposition of the elements, as every day's experience showed that the alleged chloride or bromide of ammonium was incapable of exchanging oxygen for chlorine or bromine, without losing the additional equivalent of hydrogen again in the form of water. In other terms, the decomposition of sal-ammoniac by lime, into chloride of calcium, ammonia gas, and water induced them to con-

sider this salt as a compound of ammonia and hydrochloric acid; for, in the conception of the ammonia theory, we should have to assume in this decomposition *two* consecutive changes, the transformation of the chloride into oxide, and the subsequent splitting of the latter into ammoniacal gas and water. I readily admit that the latter view is less simple, but I am inclined to think that this slight inconvenience is altogether overruled by the general advantages of the ammonium theory, especially for the purposes of instruction, by the facility with which it accounts for all phenomena of transposition and substitution, and by the simple explanation it gives of the isomorphism of the potassium and ammonium compounds, which will always be the firmest foundation of this theory. On the other hand, we have to inquire which of the two views comes nearest to the truth, and here a comparative consideration of the deportments exhibited by the compound ammoniums may be of some interest. In many respects their properties are more clearly pronounced; and their behaviour is explicit and unequivocal in those very points in which the typical ammonium leaves room for speculation. In the combination of triethylamine with bromide or iodide of ethyl, it is no longer a matter of doubt whether the ethyl leaves the iodine in order to unite more intimately with the triethylamine, for we see that the new iodide thus produced is capable of exchanging its iodine for oxygen without the newly formed oxide suffering immediate decomposition, as is the case with oxide of ammonium. On the contrary, we find this new oxide endowed with remarkable stability; although under the influence of heat it is liable to the same change which befalls the oxide of ammonium, its corresponding ammonia being reproduced. Here then in the decomposition of iodide of tetrethylammonium by metallic oxides, we are obliged by irresistible evidence to acknowledge these very two stages, the assumption of which in the analogous change of iodide of ammonium appeared to us deficient in simplicity and probability.

"The conception of ammonium does not in any way imply the notion that the different hydrogen atoms united with nitrogen in the molecules of the compound metal retain their position in the molecular system with equal persistency. We are forced by unequivocal facts to admit that the fourth atom of hydrogen is in a peculiar state of mobility, and it is on the facility with which this fourth atom is dislodged from its position that one of the foundations of the ammonia theory rests. In the compound ammoniums, the mobility of the fourth atom of hydrogen, or the hydrocarbon replacing it, still prevails, although less so than in the type itself. The decomposition of the ammonium bases under the influence of heat is particularly instructive in this respect; oxide of tetrethylammonium loses the fourth equivalent of ethyl in the form of olefiant gas and water; and this deportment might be graphically indicated by writing the formula of this compound in accordance with the ammonia theory, namely, thus

$$\left.\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} N,C_4H_5O.$$

"The iodide, accordingly, would be represented by the formula

$$\left.\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} N,C_4H_5I,$$

an expression which is, moreover, in perfect harmony with the mode in which this compound is produced, namely, by the direct union of iodide of ethyl with triethylamine.

"But now we combine the triethylamine with iodide of amyl, whereby the iodide

$$\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N,C_{10}H_{11}I,$$

is formed which, as we have seen in the preceding pages, may be converted without difficulty into the corresponding oxide; this oxide, however, cannot possibly be considered as

$$\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N,C_{10}H_{11}O,$$

for the disengagement of olefiant gas, under the influence of heat, proves to us that it is an ethyl atom, which in this compound occupies the supplemental position, if I may so call it, as represented in the formula

$$\left.\begin{matrix}C_4H_5\\C_4H_5\\C_{10}H_{11}\end{matrix}\right\}N,C_4H_5O,$$

and that the iodide, which is not likely to differ in its constitution from the oxide, has likewise to be represented by the formula

$$\left.\begin{matrix}C_4H_5\\C_4H_5\\C_{10}H_{11}\end{matrix}\right\}N,C_4H_5I.$$

"The preceding considerations clearly show, that, whatever the actual disposition of the molecules in ammonium or its congeners may be, the atoms rearrange themselves whenever the fourth equivalent of hydrogen, or of its substitute, joins the compound.

"This rearrangement, so evident in the ammonium bases containing various hydrocarbons, may be traced, moreover, in the lower ethyl bases in a very obvious manner. For as long as there is any basic hydrogen present in the ammonia skeleton, this hydrogen assumes what I have previously called the supplemental position, whenever the ammonia passes into the state of ammonium by the accession of a radicle. Bromide of ethylammonium, formed by the combination of ammonia with bromide of ethyl, when decomposed by a metallic oxide, yields ethylammonia, water, and a metallic bromide; the oxide of ethylammonium formed in the first instance being decomposed like oxide of ammonium itself. It is this very transposition which we are in the habit of representing by the equation

$$H_3N + C_4H_5Br = C_4H_5,H_2N,HBr."$$

Later researches have shown that the argument used by Hofmann, based on the behaviour of the hydroxides, is, after all, of limited value; it was first pointed out by Lossen, in 1876 (*Liebig's Annalen*, 1876, **181**, 364), that whereas the ethylated hydroxides, as a rule, lose ethylene and water when distilled, whatever the other groups

may be, in the case of the chlorides, if methyl be present, methyl chloride is usually split off.

Collie and Schryver, after studying the effect of heat on a number of mixed ammonium compounds, came to the conclusion, however, that when a mixed quaternary ammonium chloride (made from trimethylamine or triethylamine) is heated, *a mixed tertiary amine is always produced*. But the actual amount formed varies very considerably in the case of different compounds, the only product from trimethyl phenylammonium chloride, for example, being dimethylphenylamine, whilst trimethylamine is chiefly formed when allyl- and isopropyltrimethylammonium compounds are decomposed. The behaviour of the chlorides and hydroxides is also sometimes diverse: thus, whilst trimethylbenzylammonium chloride yields dimethylbenzylamine and methyl chloride, its hydroxide is resolved into trimethylamine and benzyl alcohol; but methyltriethylammonium chloride yields triethylamine, whilst the hydroxide is converted into methyldiethylamine.

The belief has gradually grown up, however, that nitrogen acts as a pentad in the ammonium compounds, and that no distinction is to be drawn such as is implied in Hofmann's reference to a supplemental position, although the evidence that this is the case is still incomplete. An important series of experiments has been made by V. Meyer and Lecco directly with the object of ascertaining whether isomeric compounds can be formed by combining, on the one hand, dimethylethylamine with ethyl iodide, and, on the other, diethylmethylamine with methyl iodide; finding the products to be identical, they came to the conclusion that the ammonium compounds are to be regarded as atomic, and not as molecular, compounds (*Liebig's Annalen*, 1876, **180**, 173).

But Lossen has pointed out that their results do not necessarily establish the correctness of their conclusion. It is possible, he thinks, that an exchange of radicles may take place during the formation of the ammonium compound. Moreover, he does not regard the fact that the products are crystallographically identical as proof that they are actually identical in structure, his argument being that two compounds such as $NMe_2Et{\cdot}EtI$ and $NEt_2Me{\cdot}MeI$ would be so similar that they would probably crystallise in isomorphous forms (*Liebig's Annalen*, 1876, **181**, 364).

On mathematical grounds, the five valencies of a nitrogen atom cannot be all similar. In the case of compounds of the type NRR'_3Cl it may be assumed, however, that the five radicles are distributed upon a sphere, and either that their mutual position is changeable, and therefore no isomerism is possible; or that the positions of the five groups are fixed, and that at least two isomerides are possible. In the case of the simpler derivatives of ammonium chloride contain-

ing hydrogen or methyl, the former view seems correct; but, in the case of derivatives containing more complicated radicles, it might be expected that, owing to their mass and size, these would not change their mutual positions so readily as do hydrogen or methyl. Le Bel is of opinion that isomerism of this kind is recognisable (*Compt. rend.*, 1890, **110**, 145). On examining a whole series of cubic mixed ammonium platinichlorides, and determining the stage at which cubic symmetry vanished, he found that whilst the trimethylpropylammonium platinichloride was still cubic, the homologous isobutyl compound was dimorphous—at first crystallising in long, highly doubly refracting forms, which change into feebly doubly refracting octahedra closely resembling cubic crystals. The chlorides from these platinichlorides were also different (*ibid.*, 1893, **116**, 513). Collie and Schryver came to somewhat similar conclusions in the case of methyldiethylisoamylplatinichloride.

Moreover, Le Bel has stated that it is possible to prepare optically active isobutylpropylethylammonium chloride (*Compt. rend.*, 1891, **112**, 724).

It is clear, therefore, that the last word has not yet been said on the subject.

* * * * *

About eight years after the publication of his researches on the ammonium compounds, Hofmann, in conjunction with Cahours, brought under the notice of the Royal Society an account of their researches on the phosphorus bases (*Phil. Trans.*, June, 1857, 575), in which they described the now familiar method of preparing trimethyl- and triethyl-phosphine by means of Frankland's zinc methyl and zinc ethyl* and phosphorus trichloride, as well as a number of phosphine derivatives, and also several phosphonium compounds corresponding in the closest manner possible to the ammonium compounds.

The history of this investigation may be traced by reference to a paper presented to the French Academy by Cahours in Hofmann's and his own names in November, 1855 (*Compt. rend.*, **41**, 831).

Hofmann, at the close of his great memoir on the amines, had not failed to draw attention to the compound prepared by Thénard in 1845 from calcium phosphide and methyl chloride as being probably the analogue of trimethylamine. Cahours, after referring to Thénard's work, points out that the subsequent discovery of stibethyl by Löwig and Schweitzer, and that of the compound ammonias by Hofmann, afforded proof that the hydrogen in ammonia and its analogues may be displaced by methyl, &c., without the loss by these

* The writer has been told by Dr. Frankland that at Hofmann's request he prepared the zinc ethyl used in the first experiments made to test the method.

hydrides of their basic properties; nay, more, that in the case of arsenic and antimony the basic properties become actually enhanced. The discovery of the tetramethyl bases of Hofmann, followed by that of the corresponding arsenic and antimony bases made simultaneously by Cahours and Riche on the one hand and Landolt on the other, had shown, moreover, that it was possible to go further and displace the four hydrogen atoms in ammonium by alcohol radicles, and that corresponding compounds of arsenic and antimony could exist. There remained but the blank between the compounds of nitrogen and those of arsenic to be filled up; and to supply this want, therefore, during a stay of a month in London, he had undertaken the study of the phosphorus compounds with Hofmann.

The monograph published by the Royal Society was the outcome of the inquiry thus initiated, which was carried out with the assistance of Dr. Leibius and Messrs. Perkin and C. Hofmann. Trimethyl- and triethyl-phosphine are fully described in it, and their perfect analogy with triethylamine demonstrated by their behaviour with the iodides of methyl, ethyl and amyl. Tetrethylphosphonium iodide is shown to resemble the corresponding ammonium iodide, and to be extremely soluble in water, but precipitable by potash. The corresponding hydroxide, whilst behaving exactly like caustic potash, and therefore resembling tetrethylammonium hydroxide, differs—it is pointed out—from the latter in its behaviour on heating, owing to the affinity of phosphorus for oxygen coming into play, yielding ethane and triethylphosphine oxide.* Lastly, attention is drawn to the extraordinary affinity of triethylphosphine to sulphur and selenium.

The analogies presented by the four elements—nitrogen, phosphorus, arsenic, antimony—as well as their peculiarities are pointed out by Hofmann and Cahours in this memoir with a clearness and precision before unknown, and in a manner which leaves no word to be said even at the present day.

The analogy between the four elements, they remark,

"Is particularly manifest in the compounds belonging to the ammonium type. In these remarkable bodies, nitrogen, phosphorus, arsenic, and antimony appear to play absolutely the same part. It is more especially in the oxides of these compound metals that analogy of composition induces a perfect identity in properties, and, indeed, of very salient properties which may be traced in almost every direction. If we were satisfied with the study of the reactions of these bodies, we should never suspect, in compounds exhibiting such a close similarity of properties, the presence of elements so

* The manner in which a number of phosphonium derivatives decompose when heated has been since carefully studied by Letts and Collie and by Collie (*Chem. Soc. Trans.*, 1888, 714).

dissimilar as nitrogen, phosphorus, arsenic, and antimony; they might, moreover, be confounded with potassa and soda, by which they are scarcely surpassed in alkaline power. Only the deportment of the hydrated oxides, under the influence of heat, distinguishes the derivatives of nitrogen from the corresponding terms of the phosphorus, arsenic, and antimony series.

"If we regard, on the other hand, the compounds belonging to the ammonia type, we observe that the electro-positive character of the substances gradually rises in intensity from the nitrogen to the antimony compounds. Thus trimethylamine and triethylamine are not capable of uniting with oxygen, chlorine, bromine, and iodine; a power which the corresponding terms of the phosphorus, arsenic, and antimony series possess in a high degree. Triethylamine unites with the acids producing compounds of the formula

$$E_3N,HCl, \quad E_3N,HSO_4, \quad E_3N,HNO_6.$$

"The corresponding compounds in the arsenic and antimony series do not exist; at all events, chemists have not yet succeeded in preparing them. Triethylamine and triethylstibine only combine directly with oxygen, chlorine, sulphur, &c., producing saline bodies which have the composition respectively

$$E_3AsO_2, \quad E_3AsCl_2, \quad E_3AsS_2.$$
$$E_3SbO_2, \quad E_3SbCl_2, \quad E_3SbS_2.$$

"In the phosphorus series, lastly, two classes are represented. Triethylphosphine not only forms compounds analogous to the salts of triethylamine, but also the terms corresponding to the binoxides of triethylamine and triethylstibine. We have, in the first place, the terms

$$E_3P,HCl, \quad E_3P,HSO_4, \quad E_3P,HNO_6,$$

and, in the second place, compounds of the formulæ

$$E_3PO_2, \quad E_3PCl_2, \quad E_3PS_2.$$

"The phosphorus compounds, accordingly, hold a position intermediat between the nitrogen compounds, on the one hand, and the arsenic and antimony series on the other. It cannot, however, be denied that the phosphorus compounds stand closer to the arsenic and antimony series than to the nitrogen group.

"Ammonia is a powerful alkali; phosphoretted hydrogen only unites with hydrobromic and hydriodic acids, whilst in arsenietted and antimonetted hydrogen the power of combining with acids has altogether disappeared. In these hydrogen compounds the gradation of properties is, indeed, much more marked than in their trimethylated and triethylated derivatives. On comparing the terminal points of the series, ammonia and antimonetted hydrogen, we cannot fail to be struck by the dissimilarity of properties which at the first glance appears to limit the analogy of the two compounds to a mere parallelism of composition. In the methylated and ethylated derivatives of these compounds, the intensity of the chemical tendencies in general is so much raised that the gradation is no longer perceptible to the same extent."

* * * * *

Hofmann devoted much attention to the study of phosphine derivatives during the three years following the publication of the

paper by Cahours and himself, presenting no fewer than 12 communications to the Royal Society, which were finally embodied in three memoirs communicated to the Society in June, 1860, entitled "Contributions to the History of the Phosphorus Bases"* (*Phil. Trans.*, 1860, 408—533). It is noteworthy that these contain accounts of a large number of crystallographic determinations by Quintino Sella, whom Hofmann terms "My friend, the celebrated crystallographer of Turin," and whose life he afterwards pourtrayed in a lengthy essay, perhaps the most remarkable and masterly of the numerous biographical notices of which he was the author; his inimitable skill in such matters is especially obvious in this case, as the subject of his memoir was not a chemist; yet he produced an account full of interest to chemists, which must rank as an enduring memorial of his remarkable versatility and literary power.

The first of the memoirs under consideration deals with the specific properties of triethylphosphine, which Hofmann speaks of as "a body in whose chemical relations the leading questions of the day are not unfrequently mirrored with surprising distinctness."

Having recounted his experience of the best method of preparing the phosphine, its oxide is fully considered. This compound exhibits in general but a slight tendency to unite with other substances; nevertheless, we are told, it affords a crystalline compound with iodide of zinc, for example, $[(C_2H_5)_3PO]_2ZnI_2$, which, strange to say, is formed in presence of a large excess of hydriodic and even of hydrochloric acid. When the anhydrous oxide is added to a concentrated solution of platinic chloride in absolute alcohol, a crystalline platinum compound is precipitated which Hofmann represents by the remarkable formula $[(C_2H_5)_3PO]_3,(C_2H_5)_3PCl_2,PtCl_4$, but to which Letts and Collie, who have prepared a similar compound from tribenzylphosphine oxide, assign the formula $4(Et_3PO),2HCl,PtCl_4$ (*Roy. Soc. Edin. Trans.*, **30**, 207). A peculiar crystalline oxychloride, $(C_2H_5)_2PO,(C_2H_5)_3PCl_2$, is said to be formed on subjecting the oxide to the action of gaseous hydrogen chloride.

The observations of most interest in the paper relate to the interaction of sulphur compounds and triethylphosphine. Although sulphur unites with triethylphosphine with the greatest readiness, and sulphide of nitrogen is instantly deprived of its sulphur by its action, sulphuretted hydrogen is without action, even in presence of air, the attraction of the phosphine for oxygen preventing the oxidation of the hydride. Mercaptan alone is also without action, but in presence of oxygen converts the phosphine into the sulphide,

* Hofmann uses the new notation for the first time in these memoirs. The preliminary communications which had been published in the Proceedings were in the old notation.

the mercaptan being reciprocally converted into alcohol. As triethylphosphine oxide and mercaptan may be placed under the most varied conditions without yielding a trace of triethylphosphine sulphide, we have to suppose, Hofmann points out, that the mercaptan interchanges its sulphur with the oxygen of the phosphine oxide only at the instant of formation of the latter; or what comes to the same thing, that the oxygen of the air, in presence of a substance so greedy of sulphur as triethylphosphine, directly takes the place of the sulphur in the mercaptan.

All attempts to displace the oxygen in triethylphosphine oxide by sulphur were unsuccessful, although the opposite change was readily effected. The different degrees of stability which characterise the oxide and sulphide are also strikingly illustrated by their behaviour towards sodium, from which the oxide may be distilled without suffering alteration, although the sulphide is reduced by it with the greatest facility to triethylphosphine.

The most remarkable of all the phosphine derivatives prepared by Hofmann, however, is the beautiful red crystalline compound of triethylphosphine and carbon bisulphide, $Et_3P{\cdot}CS_2$, which is immediately formed on bringing the two substances together*—a compound which possesses the character of a weak base. It is noteworthy that no corresponding compound is obtainable from either triethylamine or triethylstibine, or from primary or secondary phosphines, although the last two are acted on by the bisulphide.

The bisulphide compound exhibits a remarkable tendency to pass into sulphide of triethylphosphine, as, for instance, when its alcoholic solution is mixed with silver nitrate. It also decomposes in contact with water, yielding the sulphide as principal product, together with the oxide, carbon bisulphide and triethyl*methyl*phosphonium hydrate. A small quantity of a yellow crystalline substance is also formed, the composition of which is represented by the formula $C_8H_{17}PS_3$; the production of this compound was traced by Hofmann to the action of sulphuretted hydrogen, and he succeeded in preparing considerable quantities of it by digesting the red crystals with a saturated solution of sulphuretted hydrogen at 100°. It may be recrystallised from boiling absolute alcohol, although not without a certain loss; when boiled with water, it is entirely decomposed, carbon bisulphide being evolved, the solution becoming faintly alkaline. On neutralising the liquid with hydriodic acid, a sparingly soluble crystalline iodide is

* This substance is produced with such facility, and its appearance is so characteristic that its formation may be used as a test either for carbon bisulphide or for the tertiary phosphine; it is easy, as Hofmann showed, to demonstrate the presence of carbon bisulphide in coal gas with its aid, and even to use it as a means of estimating minute quantities of the bisulphide (*Ber.*, 1880, **13**, 1732).

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obtained, which has the composition represented by the formula $C_7H_{18}PSI$.

Another remarkable sulphur derivative is formed by the direct union in molecular proportions of the phosphine and phenyl isothiocyanate, two substances which interact with extreme readiness. Like those already referred to, it is a coloured substance, crystallising in uranium-yellow, monoclinic prisms. It is a well-defined base, combining with methyl iodide to form a phosphonium iodide, the hydrate from which readily decomposes into phenylisothiocyanate and methyltriethylphosphonium hydrate. Carbon bisulphide readily displaces the thiocyanate from the compound. On attempting to prepare a similar compound from phenyl isocyanate, it was found that the latter was polymerised, the phosphine remaining unaltered.

The conclusions arrived at by Hofmann regarding the constitution of these various sulphur derivatives are not without interest, although clearly in need of reconsideration in the light of modern knowledge. The red bisulphide compound was viewed by him as the primary triethylphosphonium salt of sulphocarbonic acid minus 1 mol. of sulphuretted hydrogen

$$\left.\begin{matrix}(C_2H_5)_3HP\\H\end{matrix}\right\}CS_3 - \left.\begin{matrix}H\\H\end{matrix}\right\}S = (C_2H_5)_3P,CS_2.$$

He regarded the yellow crystals formed from it by the action of sulphuretted hydrogen as derived in like manner from the triethylphosphonium salt of sulphomethylated sulphocarbonic acid,

$$\left.\begin{matrix}CH_3S\\(C_2H_5)_3HP\end{matrix}\right\}CS_3 - \left.\begin{matrix}H\\H\end{matrix}\right\}S = \left.\begin{matrix}CH_2S\\(C_2H_5)_3P\end{matrix}\right\}CS_2,$$

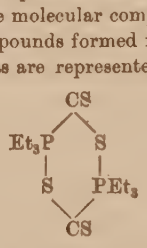
and represented the decomposition of the latter compound by water as taking place in the following manner,

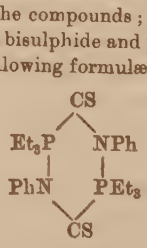
$$(CH_2S)(C_2H_5)_3PCS_2 + H_2O = CS_2 + (CH_3S)(C_2H_5)_3P{\cdot}OH.$$

He not unnaturally thought that the compound of triethylphosphine with phenyl isothiocyanate was a kind of urea.*

* * * * *

* It is open to question whether the formulæ arrived at by Hofmann in all cases represent the molecular composition of the compounds; thus, it is not impossible that the compounds formed from carbon bisulphide and phenyl isothiocyanate are cycloids such as are represented by the following formulæ—





The writer proposes to study these compounds from this and other points of view in connection with his inquiry into the origin of colour.

Hofmann's researches on the phosphine and phosphonium compounds, which followed his investigations of the monamines and the corresponding ammonium compounds, and which, as we have seen, were the direct logical outcome of these inquiries, also largely paved the way for the successful examination of the more complex derivatives obtained with the aid of compounds like ethylene bromide. The second of his three memoirs on the phosphorus bases, in fact, deals with the products obtained from this haloid and triethylphosphine, and is of particular interest, as the results were of importance in aiding him to place beyond question the nature of the interactions involved in the formation of the polyammonias generally.

His reasons for studying "polyacid" bases are stated with characteristic clearness in the opening paragraphs of the paper, and it will be of interest to quote them, as they serve to show the manner in which he was led by concurrent discoveries to thus extend his inquiries—

"In surveying the rich harvest of discoveries which of late years have rewarded the exertions of chemists, with reference to their general effect on the progress of the science, we cannot help recognising as one of the most valuable amongst their acquisitions, the development of the theory of polyatomic compounds. Seldom has a theory diffused a clearer light on previously established facts, or exerted a more fructifying and inspiring influence on the labours of chemists. First coming into notice in the chemical researches of Graham and Liebig on the polybasic acids, and afterwards extended and generalised by the experiments of Gerhardt and Williamson, it has acquired in Berthelot's beautiful investigation of glycerin a new field of discovery, the active cultivation of which has already brought to maturity a great variety of fruits. An important step in the development of these ideas was made by H. L. Buff, in showing that dibromide of ethylene can be converted into a corresponding sulphocyanate, and in the conclusions which he drew from this observation; until, in the brilliant experimental researches of Wurtz on the diatomic alcohols, the doctrine of polyatomic compounds has received its clearest and most elegant expression.

"Considering the untiring activity with which chemists have devoted themselves to the study of the polybasic acids, and, within the last few years, of the polyatomic alcohols, it cannot but appear remarkable that so little attention should hitherto have been bestowed on the polyacid bases. It is true that we are already in possession of many valuable observations relating to these bodies; but they are isolated, and the facts which they have established can scarcely be looked upon as more than accidental acquisitions. Regarded in the scientific sense as a class, and in their relations to other groups of bodies, the polyatomic bases have hitherto been left without examination."

After remarking that—

"Respecting the constitution of these compounds, and the conditions under which they would be produced, no doubt could be entertained,"

Hofmann proceeds to point out what products might be formed from ethylene bromide and ammonia or the amines; he then refers to the experimental difficulties involved in the separation and recognition of all the products of such complex interactions, and finally remarks—

'Nevertheless, the experiment with triethylamine, from which I had expected the simplest and clearest solution of my problem, did not entirely satisfy me, inasmuch as I did not succeed in obtaining more than *three* of the compounds out of the *four* which are indicated by theory. It was not indeed till I repeated the experiment in the phosphorus series, using, instead of triethylamine, the corresponding phosphorus base, that I succeeded in obtaining *all* the compounds, and that the results appeared as the pure expression of theory undisturbed by accidental products. In its reaction with dibromide of ethylene, the sharply defined characters of triethylphosphine exhibit themselves with welcome distinctness, and in the products resulting from the action, the peculiar relations between monatomic and diatomic bases become perceptible with a degree of clearness and generality such as I have never observed in any similar reaction among bodies of the nitrogen series. It is the smoothness of these reactions which renders it desirable to commence an account of a more general investigation of the diatomic bases with a description of the bodies belonging to the phosphorus series."

The primary products of the interaction of ethylene dibromide and triethylphosphine were found to be two in number, the one being *bromethyltriethylphosphonium bromide*, $(BrC_2H_4)PEt_3Br$, the other, *ethylenehexethyldiphosphoniumdibromide*, $(C_2H_4)P_2Et_6Br_2$. The former behaves in an interesting manner with silver salts and silver oxide, the oxide causing the displacement of the whole of its bromine by hydroxyl, converting it into hydroxyethyltriethylphosphonium hydrate, the compound represented by the formula, $(HO{\cdot}C_2H_4){\cdot}PEt_3{\cdot}OH$; whereas a salt, such as silver acetate, whilst readily exercising a similar effect on the one atom of bromine, more slowly induces the separation of the other atom of bromine together with an atom of hydrogen, thus giving rise to a vinyltriethylphosphonium hydrate, $C_2H_3{\cdot}PEt_3{\cdot}OH$. The bromide corresponding to this latter hydrate may be formed directly from the bromethyl bromide by heating it.

The diphosphonium compounds closely resemble the phosphonium compounds. The diiodide, for example, Hofmann points out, like most diphosphonium compounds, exhibits great stability; it melts at 231°, without undergoing the slightest change, although it is decomposed when more strongly heated over an open flame. A remarkable character of this salt is its insolubility in a moderately concentrated solution of potash; its solution, like those of the diphosphonium salts in general, is perfectly neutral. The hydrate commences to decompose at 160°, and, on raising the temperature gradually to 250°, the

whole passes over in the form of liquid and gaseous products. Hofmann arrived at the conclusion that it undergoes two principal transformations, a portion yielding triethylphosphine oxide and tetrethylphosphonium hydrate,

$$(C_2H_4)\cdot P_2Et_6(OH)_2 = Et_3PO + Et_4P\cdot OH,$$

of which the latter is ultimately resolved into triethylphosphine oxide and ethane; whilst a second portion is resolved into triethylphosphine and hydroxethyltriethylphosphonium hydrate,

$$(C_2H_4)\cdot P_2Et_6(OH)_2 = PEt_3 + (C_2H_4\cdot OH)PEt_3\cdot OH,$$

and of these the latter is at least in part converted into water and vinyltriethylphosphonium hydrate, which in turn becomes converted into ethylene and triethylphosphine oxide. A peculiar (?) molecular change precedes the actual decomposition of the dihydrate, a point being soon reached during the distillation when, on testing with platinum chloride, instead of the slightly crystalline precipitate insoluble in dilute hydrochloric acid, characteristic of the original substance, an amorphous, generally dingy yellow, precipitate is obtained, which immediately dissolves on adding a few drops of dilute hydrochloric acid. This amorphous precipitate, however, has the same composition as the crystalline ethylene diphosphonium platinichloride.

Having found that bromethyltriethylphosphonium bromide was readily converted into ethylenehexethyldiphosphonium dibromide by the addition of triethylphosphine, Hofmann prepared a large number of mixed diatomic bases of the phosphorus-nitrogen, phosphorus-arsenic and arsenic-nitrogen series by subjecting the bromethyl bromide to the action of ammonia and various monamines, monarsines, &c.; an account is given of these in the third memoir on the phosphorus bases. The compounds described resemble in the closest manner possible those produced from triethylphosphine alone; thus the hydrates of the base prepared from the bromethylphosphonium bromide and ammonia instead of behaving as an ammonium hydrate when distilled, is resolved into ammonia, water and vinyltriethylphosphonium hydrate. Hofmann also failed, in like manner, in obtaining an ethylenetetrethylphosphamine from the phosphammonium compound formed with the aid of ethylamine.

Some peculiarities are brought under notice in this memoir which deserve attention. Thus it is pointed out, that whereas trimethylamine readily combines with the bromethylated triethylphosphonium bromide, triethylamine, acting in presence of water (in alcoholic solution), merely induces the formation of the hydroxyethylated bromide, and, in the absence of water, apparently gives rise to vinyltriethylphosphonium bromide; its behaviour in this respect is analogous to that

of trimethylamine, which slowly combines with ethylene bromide, forming the compound $N(CH_3)_3(BrC_2H_4)Br$; when subjected to the further action of trimethylamine, this latter is deprived of hydrogen bromide. Again, whereas triethylarsine and the bromethylated bromide readily combine, forming the phospharsonium bromide, triethylstibine affords no similar compound; the latter also behaves irregularly with ethylene bromide, which readily acts on triethylarsine. Hofmann also refers to a peculiar behaviour of bromethyltrimethylphosphonium bromide with triethylphosphine, but without describing it. One other interesting observation should be mentioned, namely, that whereas ethylene chloride, like the bromide, readily combines with triethylphosphine, ethylene iodide is merely deprived of hydrogen iodide by the phosphine.

In a later paper (May, 1861) attention is drawn to the interesting difference in behaviour of the methylene and ethylene compounds. Methylene chloride—and also the iodide—forms first a chloromethyltriethylphosphonium chloride, a beautifully crystallised substance, which then fixes a second molecule of the phosphine. But the methylenehexethyldiphosphonium chloride produced in the latter case cannot be brought into contact with water without undergoing immediate decomposition, thus

$$(CH_2)P_2Et_6Cl_2 + H_2O = CH_3{\cdot}PEt_3Cl + POEt_3 + HCl,$$

a change taking place which, in the ethylene series, occurs only when the base is subjected to a high temperature.

Hofmann speaks of methylene dibromide behaving differently, but does not state in what way. The somewhat similar behaviour of iodoform (as well as of chloroform and bromoform) was described by him at an earlier date (October, 1859). The interaction of iodoform and triethylphosphine is of a most vigorous character; the product, which may be recrystallised from alcohol, is a triphosphonium triiodide, from which other salts can be readily prepared. The corresponding hydrate cannot be obtained, however, as reduction takes place on digesting the iodide with silver oxide, a mixture of *methyltriethylphosphonium* hydrate with triethylphosphine oxide being formed.

Carbon tetrachloride, in like manner, combines with 4 molecular proportions of the phosphine, forming a tetraphosphonium compound; but the product cannot be isolated owing to its extraordinarily deliquescent nature and the impossibility of touching it with a solvent without decomposing it; water converts it into the compound obtained from chloroform, triethylphosphine oxide and hydrogen chloride.

It is manifest that in all these cases the tendency of triethylphos-

phine to combine with oxygen (and sulphur) which distinguishes it so sharply from triethylamine, enables it to act in presence of water (or sulphuretted hydrogen) as a powerful reducing agent.

Hofmann's last communication with reference to triethylphosphine was made to the Royal Society in December, 1861; in it he describes its behaviour—as well as that of triethylamine—with chloracetic ether, which is shown to be precisely similar to that towards the alcoholic haloids previously studied. Attention is specially directed to the change that the hydrate formed from the chloride at once undergoes, losing alcohol and forming a glycocol derivative.

A long interval elapsed after the publication of Hofmann's papers on tertiary phosphines and of the phosphonium compounds derived from them, although, as he has himself remarked, the study of the primary and secondary phosphines, the examination of which promised even more noteworthy results than that of the bodies before investigated, still remained to be achieved. It is clear that the peculiar tenacity of purpose which was one of his most striking characteristics led him to bear this problem constantly in mind, for in his "New Researches on the Phosphorus Bases," communicated to the Royal Society in March 1872 (Proc., **20**, 221—239), after referring to the lapse of 12 years, he states that—

"New tasks of life have since that time presented themselves, and I have not been able to devote myself as much to research as in former days. Nevertheless, numerous attempts were made to procure the primary and secondary phosphines, which were clearly indicated by theory and partly even by M. Thénard's early observations. For a long time, however, these experiments proved unsuccessful, and it was only in the course of last summer that I at last discovered an easy method for their production."

And the manner in which the new method was discovered is stated in the following interesting passage—

"The starting point of the new series of researches was a lecture experiment. Wishing to exhibit to my class the decomposition of phosphoretted hydrogen by the spark current of an induction coil, I was unable to procure by any of the methods hitherto described, phosphoretted hydrogen of sufficient purity for this experiment. I was thus led to select a rather unusual substance as a source for phosphoretted hydrogen, namely, the beautiful compound of the latter with hydriodic acid, generally designated as phosphonium iodide. If a slow stream of water, or better, of potash or soda, be allowed, by means of a dropping tube, to flow into a small vessel containing phosphonium iodide, a regular current of perfectly pure phosphoretted hydrogen is evolved. . . The facility with which phosphonium iodide is thus seen to split up into its constituents . . . led me to think that this body might be made available for the preparation of the compounds I had so long endeavoured to obtain. Two different processes suggested themselves, both aiming at a reproduction of the conditions under which, as

I have shown now more than 20 years ago, the alcohol derivatives of ammonia are readily obtained. For this purpose it was necessary to disengage phosphoretted hydrogen in the presence of an alcohol iodide under pressure. This could be easily accomplished by submitting a mixture of an alcohol iodide and phosphonium iodide in sealed vessels to the action of an agent . . . slowly liberating the phosphoretted hydrogen from the iodide."

This anticipation was not only fulfilled, but the remarkable observation was made that on heating phosphonium iodide along with zinc oxide and an alcoholic iodide the primary and secondary phosphine were exclusively produced, although on submitting the iodide to the action of an alcohol only the tertiary phosphine and a quaternary phosphonium iodide were formed. The separation of the primary and secondary phosphine also proved to be a simple task, the salts of the former being easily decomposed by water, whilst those of the latter are stable in presence of water but immediately decomposed on adding an alkali. Besides the two methyl- and the two ethyl-phosphines, Hofmann describes in this paper the two benzylphosphines obtained by means of benzyl chloride. He subsequently described the primary and secondary isopropyl, isobutyl and isoamyl phosphines.

Benzylphosphine, like the two methyl and the two ethyl compounds, exhibits basic properties, and, like them, is at once oxidised on exposure to air, but dibenzylphosphine does not dissolve in acids, and oxygen is without action on it, even at an elevated temperature. On oxidation with nitric acid, the methyl- and ethyl-phosphines yield phosphinic acids, the primary base giving a dibasic acid, *e.g.*, $CH_3 \cdot PO(OH)_2$, and the secondary base a monobasic acid, *e.g.*, $(C_2H_5)_2PO(OH)$. Dimethyl- and the two ethyl-phosphines unite with sulphur and carbon bisulphide, but far less energetically than triethylphosphine;* as the compound of dimethylphosphine with carbon bisulphide is not crystalline, it is easy to demonstrate the absence of trimethylphosphine among the products of the interaction of phosphonium and methyl iodides.

The higher homologues of ethyl- and diethyl-phosphine closely resemble these compounds, but, as is usually the case, become less well characterised as the series is ascended. In his later papers on the subject, Hofmann describes a number of mixed phosphines and phosphonium derivatives, such, for example, as ethylisopropylisobutylphosphine and the methiodide formed from this; these were obtained by methods similar to those used in preparing corresponding

* The action of sulphur on the primary and secondary phosphines was described by Hofmann and Mahla in a paper published after his death—the last to appear in the *Berichte* bearing his name (1892, 2436). They give rise to thiophosphinic acids, such as $PSEt_2 \cdot SH$.

nitrogen compounds, by subjecting a primary phosphine to the action of an alcoholic iodide and repeating the treatment with the secondary phosphine so produced.

Attempts to prepare polyphosphines from phosphonium iodide and ethylene bromide and chloroform were unsuccessful, owing to the reducing action exerted by the hydrogen iodide, ethylene bromide giving rise to ethylphosphine and chloroform to methylphosphine.

Hofmann, however, foresaw that such compounds would be eventually produced in other ways, and, at the close of his paper, points out that a solution of phosphine in ether acts readily on iodoform, but he does not appear to have afterwards completed this investigation.

The acids obtained by oxidising the primary and secondary phosphines were shown to be readily converted into corresponding di- and mono-chlorides by means of phosphorus pentachloride, the chlorides, in the case of the methyl compounds, being well crystallised substances, which water at once decomposes.*

Although in the interval since his researches were published our knowledge of the phosphines and allied compounds has been considerably increased, chiefly owing to the discovery of phenyl derivatives by Michaelis and his pupils, in the case of this group, as in that of the amines and substituted ammonium compounds, we owe all that is fundamental to Hofmann—the properties which he has shown to be characteristic of the primary, secondary and tertiary ethyl derivatives of phosphine being characteristic of all other similarly constituted compounds.

This is true, for example, of the phenyl- and of the phenyldiethyl- and phenyldimethyl-phosphine prepared by Michaelis (*Annalen*, 1876, **181**, 265), and, in many respects, even of the triphenylphosphine discovered by Michaelis and v. Soden (*ibid.*, 229, 295). Although the latter compound, as was perhaps to be expected, is odourless, and does not combine directly with oxygen or with carbon bisulphide, it yet readily combines with sulphur, with alcoholic iodides and with chlorine, and its chloride, Ph_3PCl_2, is converted into the corresponding oxide by the action of water.

In view of these facts, it is noteworthy that triphenylstibine is incapable of combining with alcoholic iodides; that its chloride is stable in presence of water; that the hydroxide prepared by the action of alcoholic potash on the chloride, which melts at 212°, shows no tendency to lose water and form a corresponding oxide;

* Attention may be here drawn to the fact that an account of experiments with phosphonitrichloride was published by Hofmann in 1884 (*Ber.*, 17, 1909).

and that this hydroxide is readily reduced by sulphuretted hydrogen, being converted into the stibine, which apparently does not combine with sulphur.

* * * * *

After the publication of his memoir on the substituted ammonium compounds in 1851, until the commencement of his work with Cahours on the phosphorus bases in 1855, no important subject seems to have engaged Hofmann's attention, and it was not until 1858 that he began to turn his attention to the polyammonias, the first of his "Notes of Researches on the Polyammonias"—of which 24 in all were published in the *Proc. Roy. Soc.* (1858—1863)—bearing the date February 4, 1858 (*Proc.*, **9**, 150). Unfortunately, no collected account of his investigations in this field was ever published.

It is clear that the fact that the greater number of natural alkaloids contain several atoms of nitrogen, led him to study such compounds. Having referred to this in the paper in question, he states:—

"It was long my intention to extend my researches to the polyammonium bases. But my attention has been specially called to the subject of the beautiful results obtained of late, especially in France, by the study of the polyacid alcohols, by the experiments of M. Berthelot, and more particularly by the classical researches of M. Wurtz, which enable us to take a general view of this subject."

Having pointed out how a series of bases derived from two molecules of ammonia, bearing to each other the relations observed in the case of the monamines, might arise from the introduction of a dyad radicle, he calls attention to experiments made about five years before by Cloez on the action of ethylene bromide on ammonia, which appeared to show that three bases, viz., "Formylia," C_2H_3N, "Acetylia," C_4H_5N, "Propylia," C_6H_7N, were formed.

Hofmann, however, points out that it appeared probable, judging from their physical properties, that these were the diammonium compounds of which he was in search, namely, mon-, di- and triethylenediamine, and he quotes evidence proving that the acetylia of Cloez in reality had the composition of ethylenediamine. Of course, he at once proceeds to generalise, and refers to experiments made with the object of preparing triamines.

The second note (*Proc. Roy. Soc.*, April 15, 1858) briefly describes the results obtained with aniline and chloroform, by the interaction of which the *monacid* diamine, [CH(NPh)NPhH], diphenylformyldiamine, was obtained.

The next note relates to a different subject, but in the fourth (May, 1858) an account is given of the action of ethylene bromide on aniline. The product is spoken of as ethylenephenylamine, $(C_2H_4)NC_6H_5$, although the probability that it was diethylenediphenyldiamine is

clearly recognised. In a later note (the sixth) this is shown to be the case, and an intermediate compound, ethylenediphenyldiamine, is described, together with the two corresponding compounds formed from ethylamine and ethylene bromide.

Hofmann's chief reason for assuming that a diamine was formed was the observation that the product combined with methyl iodide in the proportion $CH_3I : 2C_2H_4.NC_6H_5$. The importance of this argument was dwelt on at a later stage in the inquiry (May, 1861) in the 14th note, in which the diagnosis of diamines is discussed. It is there pointed out that the residual hydrogen in each of the linked ammonia molecules is invariably affected in the same manner, the substitution of ethyl being never limited to one equivalent of hydrogen. When, however, the ammonia is converted into an ammonium compound by the action of ethyl iodide, the true nature of the substance is revealed; a monamine gives rise to only one compound, a diamine to two—tetrethylethylenediamine, for example, yielding both a pentethylated hydriodide and a hexethylated diiodide. The value of the method in cases in which easily decomposable compounds are dealt with is insisted on.

The seventh note on polyammonias (December, 1859) is in a measure controversial,* for in it Hofmann sustains the conclusions he had previously arrived at as to the nature of the action between ammonia and ethylene bromide against Cloez, who had rejected the formulæ he had assigned to the diatomic derivatives of phenylamine and ethylamine and had continued to assert that the products were monamines. After criticising his adversary's arguments, he passes to his facts and shows that the gaseous density of ethylenediamine as determined by him was that of a mixture of the anhydrous base and water formed by the decomposition of the hydrated base, and consequently that Cloez had been misled in placing reliance on the number he had obtained. He then proceeds to prove that the density of the anhydrous base was in accord with the formula he had assigned to it, whereby it was represented as a diatomic ammonia.† He shows also in this note that the compound named *acetena*mine by Cloez was diethylenediamine. As on subjecting the two bases to the action of ethyl iodide, in the one case the products were two volatile and one fixed base, and in the other one of each kind, there could be no

* In his obituary notice of Griess, who helped him in this inquiry, Hofmann observes that—"Few who now use ethylenediamine and diethylenediamine remember that it required a long controversy with Cloez to secure for these compounds the recognition of the position in the system of organic chemistry which they now occupy."

† A further account of observations in explanation of the "anomalous" vapour density of the hydrated base is to be found in the ninth note.

doubt as to the accuracy of the conclusions arrived at—and the manner in which he sums up his case, towards the close of the note, shows that he is convinced of this—

"In the present state of science we rely upon a certain number of considerations which guide us in the construction of a chemical formula. These are—the study of the origin of a body; analysis; observation of the physical properties, and, especially of the boiling point; the determination of the vapour density; and lastly, the examination of its metamorphoses. I have endeavoured to look at the question under discussion from these several points of view; experiment has invariably given the same reply."

A more concise statement of procedure could not be made.

The conclusion is pointedly stated in this note that "it follows from this controversy that the diatomic alcohols imitate the monatomic in their deportment with ammonia;" in other words, that a series of bases exist related to glycol in the same way that the three ethylamines are related to ethyl alcohol.

Meanwhile, the attempt was being made to associate a still larger number of ammonia molecules. Thus, in the fifth note (June, 1858), we find a description of the action of carbon tetrachloride on aniline, which is shown to give rise to the triamine, $C_{19}H_{17}N_3 = C(NPh)(NPhH)_2$, now known as triphenylguanidine.

In discussing the relations between the monatomic and polyatomic bases towards the close of his researches on the phosphorus bases (*Proc. Roy. Soc.*, **10**, 619), Hofmann fully considers the many ways in which diatomic bromides may act on bases to form polyatomic bases of a higher order; and the following eminently characteristic sentence occurs at the close of the paper—

"I have but a faint hope that I may be able to trace these new paths in the numerous directions which open in a variety at once tempting and perplexing. Inexorable experiment follows but slowly the flight of light-winged theory. The commencement is nevertheless made, and even now the triammonium and tetrammonium compounds begin to unfold themselves in unexpected variety. One of the most remarkable compounds belonging to the triammonium group is *diethylenetriamine* . . . This base, *the first triacid triammonia*, forms splendid salts . . . ."

The description of the base was given about a year later in the 16th note on polyammonias, but only in the briefest terms. It is present, together with triethylenetriamine, in the portion boiling at 200—220° of the mixture of bases obtained on heating ethylene bromide with ammonia. They form a great variety of salts, most of which crystallise with facility; their separation was chiefly effected in the form of chlorides, bromides and iodides, or of platinum salts and gold salts. Both are described as powerfully alkaline liquids, soluble in

every proportion in water and alcohol, but which do not exhibit the tendency to form definite hydrates so pronounced in the diamines.*

A subsequent note (the 17th) contains an account of the di- and tri-ethylenetriethyltriamines obtained from ethylamine and ethylene bromide; these closely resemble the ethylenetriamines, exhibiting the same tendency to form diatomic salts.

A still higher stage is reached in the next note (the 18th), which is devoted to tetrammonium compounds, several of which formed from ammonia, ethylamine and diethylamine respectively and ethylene bromide are described; the octethylated tetrammonium compounds derived from diethylamine are remarkable for their definite characters, being still crystalline.† But it must be confessed that, except as affording proof that a series of polyammonias can be produced corresponding with the polyethylenic glycols obtained by Wurtz, the various substances described offer few points of novelty or interest. Indeed, the following words used by Hofmann, in the course of the note under consideration—

"As a chemical theory expands and becomes more and more consolidated, the interest attached to the individual compounds used as scaffolding in raising the structure become less and less, diminishing in fact in the inverse ratio of the number of compounds which the theory suggests,"

may not inappropriately be applied to the separate results of his inquiry into the polyammonias; and the fact that they were never published in a collected form is perhaps ascribable to his having recognised that in such a case it was unnecessary to put details on record.

Ethylenediamine was prepared on a large scale by Hofmann in 1872 with the aid of ethylene chloride formed in the manufacture of chloral, and its properties were more fully studied, especially with the object of contrasting its behaviour with that of the primary monamines (*Proc. Roy. Soc.*, **20**, 425).

His attention being thus re-directed to the diamines, he was led also at this time to prepare propylenediamine (*Ber.*, 1873, 308). This was found to boil only 3° higher than ethylenediamine, and, like the latter, to attract moisture with most remarkable avidity.

* The formation of these hydrates again occupied Hofmann's attention in 1873. In a note on propylenediamine (*Ber.*, **6**, 311), after referring to the fact that ethylenediamine which has been dried by prolonged digestion with caustic potash still retains a molecular proportion of water (he had described it in 1860 as forming a beautiful crystalline, very stable hydrate—*Proc. Roy. Soc.*, **10**, 597), he points out that when the propylene compound is similarly treated, two molecular proportions retain only one molecular proportion of water.

† The production of what appears to be even higher terms, yielding amorphous salts, was referred to by Hofmann in 1870 (*Ber.*, **3**, 762).

It is clear that the subject continued to interest him, as he published a number of communications, as late as 1890, describing the various amines prepared with the aid of ethylene chloride, especially diethylenediamine, diethylenetriamine and triethylenetetramine; having obtained diethylenediamine—now recognised as a cycloid—in the crystalline state, he was led to identify it with the commercial product first sold as spermin and afterwards as piperazine (*Ber.*, 1890, 3297, 3711, 3723).

All the researches on the polyammonias to which reference has thus far been made concern ethylene derivatives. That Hofmann, however, "had repeatedly endeavoured to produce the diatomic bases corresponding to the aromatic amines" we can well believe. As he points out in his 19th note (December, 1861), the method for producing such compounds appeared obvious, the idea naturally presenting itself to look to dinitrobenzene as the source from which phenylenediamine might be obtained; in fact, it seemed very probable that the nitrophenylamine which Muspratt and he had prepared was but the first product of reduction, and that prolonged treatment would lead to the complete reduction of the dinitro-compound. All such attempts were unsuccessful, however.

Hofmann's attention, he tells us, was drawn again to the study of the aromatic diamines under peculiar circumstances—by his receiving a specimen of a crystallised base, obtained as a secondary product in the aniline works of M. Ch. Collin, of Paris. This proved to have the composition of tolnylenediamine, and obviously owed its origin to the presence of toluene in the commercial benzene used in preparing aniline. Finding that dinitrotoluene was easily reduced by means of iron and acetic acid—

"The method of reduction now generally adopted in the manufacture of aniline—the behaviour of the dinitro-compounds of the homologues of toluene, especially dinitrobenzene, was at once examined—with the result that phenylene diamine (meta) was discovered."

The closing words of this note, in which Hofmann refers to MM. Collin and Coblentz (the chemical director of the works) for the materials placed at his disposal, are not only strikingly characteristic of his style, but also expressive of an important truth which is not always sufficiently recognised—

"By facilitating the scientific elaboration of the new diatomic compounds, these gentlemen have endeavoured most gracefully to acknowledge the debt of gratitude which the aniline industry owes to theoretical inquiries in organic chemistry."

Equally graceful is the manner in which, on another occasion, he

returns his thanks for the beautifully crystallised cyanine placed at his disposal by M. Menier—

"Though proud of her office as guide of industry, science acknowledges without blushing that there are territories on which she cannot advance without leaning on the strong arm of her powerful companion. Joint labours of this kind cannot fail to seal the pledge of alliance between industry and science."

But little more remains to be said of his researches on the poly-ammonias. Two of the notes refer to the discovery of new bases among the secondary products of the manufacture of aniline, viz., paraniline, $C_{12}H_{14}N_2$, and martylamine or xenylamine, since recognised as paramidodiphenyl. One relates to the discovery of hydrazobenzene as an intermediate product in the formation of benzidine from azobenzene; and another to the production of (para)phenylenediamine from the nitraniline obtained by nitrating acetanilide, this being the last of the notes on poly-ammonias.

But it must not be forgotten that the colouring matters produced from aniline were recognised by Hofmann as poly-ammonias, and probably the most important of all his notes on such compounds is the 20th (*Proc. Roy. Soc.*, Feb., 1862, **12**, 2), in which he gives the results of his analyses of rosaniline and its salts. The name rosaniline was felicitously chosen by him

"To commemorate the origin of the compound in its name, since it appeared to be the prototype of a number of similar substances obtainable by similar processes from the homologues, and probably also from the analogues, of aniline."

Nicholson, who first obtained the base and its salts in the state of purity, had termed it roseine.

Beyond defining rosaniline as a triacid triamine, Hofmann was unable to offer any opinion regarding its constitution; but it is clear that he foresaw that such compounds were of a different order from those he had previously studied. In fact, a few months later, when discussing the nature of cyanine, he remarks that—

"The theory which (in 1852) satisfactorily represented the constitution of the nitrogen bases then examined, requires an expansion to include the tinctorial ammonias added to our knowledge during the last decade. The time for the enunciation of this amplified theory has not yet arrived."

Nor did it fully arrive until many years later—not until 1876—when Emil and Otto Fischer began the publication of the remarkable series of observations which led them to discover the relation of rosaniline and its congeners to the hydrocarbon triphenylmethane—a research of the utmost importance in relation to both theory and

practice. But in the interval, a very large amount of valuable work had been done by Hofmann as well as by others which all contributed to the solution of the problem. It should especially be mentioned, that the study of the behaviour of rosaniline with nitrous acid, to which Hofmann first drew attention in 1862, practically gave the clue to its composition.

* * * * *

The attempt has been made in the course of the foregoing account to broadly trace the gradual development of Hofmann's researches on amines and ammonium compounds and the allied phosphorus derivatives, the record of which necessarily forms the chief chapter in a history of his scientific labours. At the time of his departure from England, he had practically completed his studies of this class of compounds; indeed, with the notable exception of the research on primary and secondary phosphines, almost all of his contributions to our knowledge of the chemistry of aminoids—including those on colouring matters, of which Dr. Perkin has given so interesting an account—were the outcome of work done during a period of less than 20 years in the modest quarters and with the modest appliances afforded by the Royal College of Chemistry in Oxford Street, the exterior of which is shown in the figure opposite.

The building had a frontage of only 34 ft., its depth being 53 ft. The whole of the first floor was occupied by the students' laboratory, the bench at which the seniors worked being in front of the upper row of windows seen in the figure. On the ground floor, the space on the right of the hall passage was devoted to the Professor's use as a private laboratory, his private room being on the left at the back of the building; the room in front was the balance room and library. The basement was used for larger and rough operations, and contained furnaces, a steam boiler, &c. The lecture theatre was built out at the back. The porter kept apparatus for the use of students, chemicals, &c., in the cellars under the street pavement.

But the record of his activity as an English Professor would be altogether incomplete, and the extent of his services to chemical science would not be sufficiently indicated, if some reference were not made to other work emanating from the Oxford Street laboratory.

Hofmann, as Dr. Perkin reminds us, was practically the discoverer of benzene in coal tar. We must go back fully 50 years to find the record of the discovery in a modest note in *Liebig's Annalen* (September, 1845, **55**, 200), "Ueber eine sichere Reaction auf Benzol; von Dr. Aug. Wilh. Hofmann, Privatdocenten der Chemie an der Universität, Bonn."

The reaction described consists in converting the benzene into nitro-

benzene, then reducing by means of acid and zinc,* and testing for the aniline with bleaching solution. It is shown that a single drop suffices for the test, and that in this way it is possible to detect the presence of benzene in a variety of products.

Events, as we know, have proved the discovery to be one of enormous practical importance; the following passage, in which it is recorded, is therefore of interest—

"Man findet vielfach in Abhandlungen und Lehrbüchern angegeben, dass das Steinkohlentheeröl Benzol enthalte, allein es ist mir keine Untersuchung bekannt geworden welche sich direkt mit dieser Frage beschäftigt hätte. Von meinen Versuchen über die organischen Basen des Steinkohlentheeröls her, besass ich noch eine Quantität der leichten Kohlenwasserstoffe welche bei der Rectification des rohen Destillationsproduktes des Steinkohlentheers zuerst übergegangen waren. In diesem Oele muste das Benzol enthalten seyn, wenn sich bei der Destillation der Steinkohle überhaupt welches bildet. Ich unterwarf diese Flüssigkeit zu dem Ende einer neuen Destillation; sie gerieth bei 105° ins Sieden, der Siedepunkt stieg aber fortwährend noch höher. Ich sammelte was bis 118° überging und rectificirte das Destillat von Neuem; es begann jetzt schon bei 94° zu sieden und der Siedepunkt stieg weit langsamer als zuvor. Was bis zu 105° überdestillirte wurde dem Versuch unterworfen; es liess sich mit Leichtigkeit erkennen, dass diese Flüssigkeit eine grosse Quantität *Benzol* enthielt."

Hofmann was not the man to leave such an observation unexploited, especially when the necessity of obtaining aniline for his researches pressed upon him, and although he did not personally undertake the investigation, it was in the Oxford Street laboratory that Mansfield, a few years afterwards, carried out his memorable "Researches on Coal Tar" (*Chem. Soc. J.*, 1849, **1**, 446), which were attended with so tragic an end—researches which, he tells us, were commenced at the request of Hofmann and conducted under his advice. The investigation appears to have been the first in which the separation of a constituent of a mixture of liquids by fractional distillation was promoted by using a still head kept at a temperature below the boiling point of the less volatile constituents.

Mansfield not only separated benzene from coal tar, but showed how it might be readily prepared on a large scale of any desired degree of purity, of course availing himself of Faraday's previous

* Hofmann appears to have been the first to use a metal together with an acid as a reducing agent, and to recognise the value of "nascent" hydrogen as a means of reducing nitro-compounds. Bechamp's discovery of the use of ferrous salts as reducing agents was not communicated to the French Academy until July 1854, and the use of iron and an acid was described soon afterwards by him in the *Annales de Chimie*. Such being the case, it is remarkable that the discovery of aromatic diamines was not more easily made by him, and that instead of attempting to reduce dinitrobenzene by means of sulphuretted hydrogen only, he did not at once try other reducing agents.

observations. He at the same time pointed out that it might be procured to any extent from coal tar, or from the light naphtha, in which, he said, it had hitherto been "wasting its sweetness on the desert air;" and that the promises which it made of utility were sufficiently numerous to encourage a belief that it might form a special object of manufacture and of commerce.

But the study of his paper promotes mixed feelings. In the introductory portion, in which an account is given of previous investigations of products of destructive distillation, after referring to the dearth of knowledge of coal tar products, he remarks—

"It appears somewhat strange that, in this country, where coal tar is so exceedingly plentiful, our chemists should have been contented with the discovery of naphthalene, and should have allowed others less fortunate than ourselves in being able to command abundance of this almost national production, to inform us of the existence at our feet of vast quantities of aniline, of paranaphthalene, and of other remarkable substances; and it appears, perhaps, no less singular that we should have failed as yet in applying them, when discovered, to the practical uses which they will, no doubt, some day claim."

It is in the highest degree remarkable that an aniline colour industry so soon afterwards came into existence and acquired such importance here; that an industry of corresponding magnitude was in consequence founded on Mansfield's researches; that an anthracene industry subsequently arose; and, lastly, that the azo-colour industry, although conceived, we must allow, in the Marburg laboratory, yet passed through its whole period of gestation—first in the College of Chemistry and then in an English brewery—and sprang into being in this country. The record is a glorious one. For a time, at least, we were not open to the reproach conveyed in Mansfield's words, especially during Hofmann's presence among us. But how different is the condition of affairs now. It is fast becoming necessary to go back to the dim records of the past for an account of English victories in such fields; the men who gained them are all but gone, without leaving successors worthy of the name. Hofmann, Griess, Simpson, Maule and Nicholson have no modern English equivalents; but the type has not merely been preserved but multiplied and even improved abroad. Perkin alone we rejoice to retain among us, and still more that he has retired into a higher sphere of usefulness.

Yet coal tar may still be characterised in Mansfield's words as a national production, and it is an appalling fact, that after having successfully established such industries, we should have allowed them largely to slip through our fingers, in consequence of the failure of our industrial chiefs to march with the times. Nor must we forget that Hofman himself warned us at the very outset, when—foreseeing,

it would seem, what would be the course of events—he insisted upon the importance of cultivating natural science in its bearings upon the whole mechanism of society, as the mainspring both of industry and national prosperity, and, in Humboldt's words, pointed out the fate in store for those who neglected to fully apply science to manufactures.

And it is more than strange, not merely "somewhat strange," that we should have contributed so little, since Mansfield's time, to the knowledge of the chemistry of coal tar, a branch of our subject which has been cultivated with the utmost zeal and success elsewhere.

Mansfield clearly established the existence of toluene, as well as of benzene, in coal tar; he also separated a fraction boiling at about 140—145°, which he suggested might prove to contain cumene identical with that from cuminic acid; and another fraction, boiling at 170—175°, which it was thought might be cymene. It is in no way surprising that he should have failed in obtaining more definite results. From the experience since gained we know that it is impossible to separate any other single substance besides benzene and toluene from coal tar naphtha by mere distillation, owing to the presence in it of a variety of isomeric benzenes of nearly the same boiling point, as well as of paraffinoids and unsaturated hydrocarbons of several series. It was not, in fact, until Fittig and Tollens devised synthetic methods of preparing the benzenes, similar to those used long before by Frankland and by Wurtz, that their properties became sufficiently known to permit of their recognition in the naphtha; and another long interval elapsed before the isolation of the separate modifications was successfully accomplished by Jacobsen through the agency of sulphonic acids.

Even the relation of toluene to benzene was not established until 1864, when Fittig and Tollens prepared the hydrocarbon from bromobenzene, methyl iodide and sodium (*Liebig's Annalen*, **131**, 303); Fittig and Tollens, in fact, engaged in their research in the expectation of obtaining hydrocarbons which *might perhaps* prove to be identical with the homologues of benzene. Kekulé's luminous exposition of the nature of benzene—the bright spot around which all other discoveries relating to benzenoid compounds, the characteristic and essential constituents of coal tar, must ever centre—was not published until 1865.

We now know that the naphtha contains besides benzene and toluene—not to mention thiophene, the very shadow of benzene, as Victor Meyer has shown in the course of his classical researches—the three dimethylbenzenes and ethylbenzene, of which the last, however, has not yet been actually isolated, 1 : 2 : 4- and 1 : 3 : 5-trimethylbenzene, and 1 : 2 : 4 : 6-tetramethylbenzene. Numerous solid

polycycloid hydrocarbons have been separated from higher fractions of the tar. Whilst some few of the products in tar are formed by the breaking down of benzenoid compounds present in coal, there is little doubt that the majority of its constituents are products of synthetic changes occurring at high temperatures, but our knowledge on these subjects is very vague at present.

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Before passing from the hydrocarbons it should be pointed out that we owe a not inconsiderable part of our knowledge of one of the homologues of benzene, viz., 1 : 3 : 5-trimethylbenzene or mesitylene, to Hofmann, who examined it long before its existence in coal tar was recognised; in fact, this only dates from 1869, when Fittig and Wackenroder showed that coal tar cumene was a mixture of the two trimethylbenzenes we now know to be the 1 : 3 : 5- and 1 : 3 : 4-modifications. Sir R. Kane, who first obtained mesitylene by distilling acetone with sulphuric acid, had represented it by the formula C_6H_4, which at a later date was doubled by chemists on evidence afforded by vapour-density determination made by Cahours. Hofmann (*Chem. Soc. J.*, 1849, **2**, 104) drew attention to the fact that the boiling point of mesitilole (as he terms it—no doubt, in order to harmonise its name with that of benzole) was much higher than that a hydrocarbon $C_{12}H_8$, containing the same number of carbon atoms as benzene, would be likely to possess, and inferred that the true formula was $C_{18}H_{12}$ (C_9H_{12} in our present notation), from the fact that when subjected to the action of moderately concentrated nitric acid the hydrocarbon gave a nitro-derivative (dinitromesitylene) convertible by reduction into a nitromesidine the formula of which could only be deduced from that of a hydrocarbon of the formula $C_{18}H_{12}$. Tribromomesitylene and mesitylenesulphonic were obtained for the first time in the course of this work.

This communication affords another illustration of the uncertain state of belief in which chemists were then plunged regarding vapour densities, and serves to emphasise the value of Canizzaro's services in this connection, for, referring to Cahours's determination of the vapour density of the hydrocarbon, Hofmann remarks—

"If this determination be correct, one equivalent of mesitilole would represent not less than 6 volumes of vapour, a number which has never been observed in any similar case. All the well investigated hydrocarbons have given hitherto 4 volumes. It is possible that the specific gravity of the mesitole vapour is subject to similar variations as have been observed with acetic, butyric, valerianic acids, and several other compounds; it is possible, likewise, that an equivalent of mesitole is actually represented by 6 volumes of vapour, and this anomalous condensation may assist in explaining the difference between the constitution of this body and cumole, which, like the other hydrocarbons, contains only 4 volumes of vapour. Be this, however,

as it may, the subject requires further investigation. I have hitherto been prevented repeating the determination of the specific gravity from not having obtained the hydrocarbon of a perfectly constant boiling point."

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Among the services rendered by Hofmann there is one which should be referred to before passing to other subjects, as it has been of immense value not only in the laboratory but especially in working on the large scale, simple though it be, viz., that recorded in the following passage in the paper on the preparation of nitraniline by Muspratt and Hofmann communicated to the Society in March 1846 (*Chem. Soc. Memoirs*, **3**, 119)—

"For our research we had to prepare a large quantity of dinitrobenzol. The transformation of nitrobenzol into dinitrobenzol proceeds very slowly, even when it is boiled repeatedly with the strongest nitric acid. It is obtained, however, very speedily by dropping benzol or nitrobenzol into a mixture composed of equal parts of fuming nitric acid, and concentrated sulphuric acid, as long as the liquid remains homogeneous."

The use of sulphuric acid in nitrating benzene, it is well known, is of the first importance as enabling the operation to be effected in an economical manner; and in many cases nitration is only possible in its presence, owing to the occurrence of oxidation when nitric acid is used alone: the manufacture of gun-cotton and of nitroglycerin are cases in point. There is good reason to suppose that the sulphuric acid has a definite determinative effect on the course of the change, and that it does not merely serve to maintain the strength of the nitric acid (compare *Chem. Soc. Proc.*, 1891, 89).

Another important practical step taken by Hofmann consisted in using acetanilide for the preparation of derivatives of aniline. For an account of this reference must be made to a paper by Mills, then one of his students (*Proc. Roy. Soc.*, 1860, **10**, 589), describing the preparation of brom- and chlor-aniline. Hofmann explains, in a footnote, how Arppe's observation that tartronitrophenylamide, when hydrolysed, gave a nitraniline (para-) isomeric with that obtained from dinitrobenzene had led him to "nitronate a more easily procurable phenyl compound, viz., acetylphenylamide," the result being that he found it could be used with considerable advantage. On this occasion he took the opportunity of pointing out that the dinitromelaniline he had prepared 10 years previously also gave the nitraniline isomeric with that from dinitrobenzene when hydrolysed.

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There is abundant evidence that Hofmann at all times took the keenest interest in current problems unconnected with his own special researches, displaying great judgment in their discussion. Thus in a brief postscript to a paper by Field on the formation of cumonitrile

(*Liebig's Annalen*, 1847, **65**, 56), he refers to experiments on the preparation of butyronitrile and valeronitrile which he had been induced to make in consequence of the observations of Frankland and Kolbe on the intimate connection of the nitriles with the cyanides of the organic radicles, a discovery which we know excited the greatest interest at the time.

A later communication (*Chem. Soc. J.*, 1850, **3**, 121) entitled a "Note upon the Action of Heat upon Valeric acid, with some Remarks upon the Formulæ of the Alcohol Radicles"* is devoted to the discussion of the views of these same chemists on the molecular composition of the alcohol radicles, and deals, therefore, with one of the most important fundamental questions of chemical theory. The hydrocarbons obtained by Frankland from the alcoholic iodides by the action of zinc and described under the names methyl, ethyl and amyl, were, as all know, at first regarded as the actual radicles; but, as Hofmann tells us, Laurent and Gerhardt pointed out in a report to the French Academy on Frankland's work that they might with more probability be considered as homologues of marsh gas. He very fully discusses the two points of view, and with great acuteness strongly advocates the latter; the concluding paragraph of the paper may be quoted as an illustration of the foresight he displayed—

"Should experiment, however, prove that the so-called alcohol radicles are actually the homologues of marsh gas, as supposed by Messrs. Laurent and Gerhardt, these substances, although losing the prestige of radicles in the conception of the electrochemical theory, would certainly not present less interest. Chemists know the remarkable manner in which the researches of Dumas, Regnault, and Melsens have linked the methyl series to marsh gas, and the facility with which we pass from marsh gas over to chloride of methyl. We have a right to expect that the higher homologues of marsh gas will exhibit a similar deportment. If this be actually the case, the action of chlorine upon ethyl would place the whole series of the butylic alcohol at our disposal; in fact, we should have discovered a general method of forming the homologues of common alcohol, and this series, presenting as yet so many gaps, would ere long be as complete as the parallel group of the fatty acids."

It was in the hope of passing from the nitriles to the alcohols, doubtless with the object of completing the series, that Buckton and Hofmann were led to subject the nitriles to the action of sulphuric acid (*Phil. Trans.*, 1856, 453—480). They anticipated that the interaction would resemble that of hydrogen cyanide and sulphuric

* This follows an account by Captain Reynolds on the preparation of propylene by passing amyl alcohol through a red-hot tube. It is of interest, historically, that Reynolds speaks of the name propylene as being, "like the rest of the series, derived from the corresponding alcohol, in this case still unknown, and for which the appellation of propylic alcohol has been suggested by Dr. Hofmann."

acid; that acetonitrile, for example, would yield carbonic oxide and the acid sulphate of methylamine, just as carbonic oxide and the acid sulphate of ammonia are formed from hydrogen cyanide; instead, however, of such products, they obtained the sulphonic acid of the acid corresponding to the nitrile, and disulphonic acids formed by the displacement of the carboxyl group when the action of the acid was prolonged.

These results led Hofmann to instigate experiments on the action of sulphuric acid on anisic and salicylic acids; those with the former acid were carried out by Žervas, who obtained sulphanisic and anisoldisulphonic acids, whilst Duppa prepared similar derivatives from salicylic acid (*Chem. Soc. J.*, 1857, **10**, 211; *Proc. Roy. Soc.*, 1857, **8**, 495).

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But one research on alcohols can be directly connected with Hofmann's name, that on allyl alcohol, which he carried out in conjunction with Cahours (*Phil. Trans.*, 1857, 575—600). Shortly before this was commenced, Berthelot and de Luca, by subjecting glycerin to the action of phosphorus iodide, had obtained "iodopropylene," from which they—and also Zinin—had prepared a sulphocyanate identical with natural oil of mustard; Redtenbacher had previously prepared acrolein and acrylic acid, and the relation of these compounds to the oils of garlic and mustard had been established by the observations of Will and Wertheimer, and of Berthelot and de Luca; bromopropylene had been prepared by Captain Reynolds in Hofmann's own laboratory, and he had himself prepared chloropropylene: an almost complete series of derivatives of the radicle C_6H_5* was therefore known. But, to quote a passage from the joint paper, which clearly bears the impress of Hofmann's style—

"There yet remained the keystone to be inserted into this edifice; in other words, there was to be discovered the alcohol to which not only all the preceding compounds could be referred, but which might serve in producing a long series of substances analogous to the host of compound ethers derived from common alcohol."

Hofmann and Cahours fully describe the preparation and properties of allyl alcohol and of a considerable number of allyl derivatives, among others the sulphide, which they show to be identical with natural garlic oil.

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Hofmann (in conjunction with Cahours) was not only the discoverer of an unsaturated alcohol which was the first of its kind, and to

* Called *allyl* for the first time, in their communication, by Hofmann and Cahours.

which special interest still attaches on account both of its relation to glycerol and the very limited number of such alcohols; he also discovered sorbic acid, $C_6H_8O_2$, a crystalline, unsaturated acid of the $C_nH_{2n-3}.CO_2H$ series, which has since been the subject of much interesting inquiry. This acid was prepared from the volatile oil obtained on distilling unripe mountain ash berries with steam (*Chem. Soc. J.*, 1860, **12**, 43); judging from Fittig and Barringer's observations (*Liebig's Annalen*, 1872, **161**, 307), the oily parasorbic acid which Hofmann separated from the crude oil by distillation, and which was converted into the crystalline acid by alkalis and acids, was but impure sorbic acid, and not an isomeride, as was long supposed.

An observation of interest to which he drew attention in 1850 (*Chem. Soc. J.*, **3**, 181) should be here referred to, viz., that cinnamic acid, unlike its inferior homologue, benzoic acid, passes unchanged through the animal system.

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The observation which led Griess to his great discovery of the diazo-compounds was made in Kolbe's laboratory in Marburg, and was briefly described in *Liebig's Annalen* (**106**, 123) early in 1858, under the title "Vorläufige Notiz über die Einwirkung von Salpetriger Säure auf Amidinitro- und Aminitrophenylsäure." But the paper in which he first drew attention to the fact that he had established a *new mode of reaction* of nitrous acid was communicated to the Royal Society on December 9, 1858, by Hofmann, whose assistant he then was, the term diazo-derivative being here used for the first term. Although, as Hofmann has told us, the latter paper was a translation of that in the *Annalen*, it is distinctly more explicit. Hofmann may be said to have himself almost missed the discovery of the peculiar behaviour of primary benzenoid amines towards nitrous acid, as his attention was directed to its action on aniline as early as 1850 (*Chem. Soc. J.*, **3**, 231). Sterry Hunt had stated in 1849 that nitrous acid converted aniline into phenol, but his experiments were only of a qualitative character. Hofmann repeated his observations and confirmed them, but only succeeded in obtaining satisfactory results by using aniline hydrochloride and silver nitrite. On subjecting aniline mixed with nitric acid to the action of nitric peroxide, in the manner originally proposed by Piria—who was the first to submit amido-compounds to the action of nitrous acid—he obtained a brown, resinous mass, from which, however, he separated the till then unknown (ortho)nitrophenol, the properties of which he more fully described several years afterwards (*ibid.*, **10**, 203). A number of observations on the action of nitrous acid on ethylamine and its homologues are recorded in this paper.

In the course of his researches on the polyammonias (*Proc. Roy.*

Soc., 1860, **10**, 495), Hofmann made use of the "beautiful mode of substituting nitrogen in the place of hydrogen, lately discovered by P. Griess," at the time when he was seeking for benzenoid diamines, in studying the compound Gottlieb had prepared by partially reducing dinitraniline, then known as nitrazophenylamine, but which, in his opinion, was probably a nitrophenylenediamine, a view confirmed by the result he obtained. It is noteworthy that the product—as Hofmann pointed out—differed in many respects from those obtained in a similar way from other nitrogenous substances, especially in exhibiting remarkable stability; this is readily understood now that we are acquainted with condensation products formed from orthamidodiazo-compounds.

In a note on isatin, published in 1861 (*Chem. Soc. J.*, **13**, 73), attention was drawn by Hofmann to the extreme facility with which this substance is converted into nitrosalicylic acid by nitrous acid.

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It will be remembered that, in his earliest research, Hofmann made an important use of chloranil (tetrachloroquinone) in establishing the identity with aniline of the substances described as benzidam, &c. In his second paper he tells us that he was induced by—

"The close relation subsisting between the aniline and phenyl series to try whether chloranil could not be obtained from different members of this group of bodies. . . ."

Phenol, and a number of other substances, were subjected to the action of hydrochloric acid and chlorate of potash. It is noteworthy that the production of chloranil from phenol in this manner was described in a paper read to our Society on December 2, 1844 ("Remarks upon Chloranil," *Chem. Soc. Memoirs*, **2**, 226), which was the first he communicated to us. Attention may be directed to the final paragraph of the paper, as it shows that he had not only recognised the relation of chloranil to quinone, but had also formed views as to the relationship of the latter to aniline—

"In concluding, I wish to call the attention of chemists to the application of chlorate of potash as an oxidising agent, for up to the present time it has been but seldom employed in organic chemistry, and yet the study of its action might, in many cases, lead to very remarkable results. I have treated *kinone*, which has lately become so interesting, in a similar manner to what has been stated, and found that it was transformed with the greatest facility into chloranil. In a future paper this subject will be examined more closely, and at the same time I shall throw out some hints concerning the relations of kinone to aniline, a base from which it can likewise be produced."

The promise here made was never fulfilled. It is somewhat remarkable, therefore, that almost the last paper Hofmann published before

leaving England was a "Note on Kinone" (*Proc. Roy. Soc.*, 1863, **13**, 4). In this he pointed out that quinone was easily formed on oxidising (para)phenylene diamine; and that aniline gave an appreciable amount of quinone on oxidation, and benzidine a theoretical yield. The action of aniline on quinone and on chloranil was studied by him at this time, and the results he obtained in the latter case led him to correct Hesse's previous observations on the subject.

Baeyer having suggested that quinone might be derived from 2 mols. of benzene, Hofmann was led to determine its density, and to prove for the first time that it was correctly represented by the formula $C_6H_4O_2$ (*Ber.*, 1870, **3**, 583).

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Hofmann's contributions to inorganic chemistry were remarkably few. In this connection a note may be referred to "Sur le Bromure de Titanium" (*Compt. rend.*, 1856, **42**, 352), in which the preparation of this substance by Duppa is recorded. It is one only of a number of instances in which Hofmann's interest in Kopp's generalisations on boiling points is manifest. The note also serves to recall the time when the atomic weight of silicon was undecided, and its chloride bore the formula $SiCl_3$.

In describing the use of pentachloride of antimony in the preparation of chlorine compounds as a carrier of chlorine (*Chem. Soc. J.*, 1861, **13**, 62), he drew attention to the remarkable action of this substance on carbon bisulphide, from which it simply displaces the sulphur in the manner represented by the equation $CS_2 + 2SbCl_5 = CCl_4 + 2SbCl_3 + 2S$, a small quantity only of sulphur chloride being formed by the action of the pentachloride on the separated sulphur.

He by no means neglected analytical chemistry. The method used in qualitative analysis of separating cadmium from copper, based on the solubility of cadmium sulphide in dilute sulphuric acid, was devised by him. The separation of arsenic from antimony also engaged his attention (*Chem. Soc. J.*, 1861, 78). A number of complete analyses of English mineral waters were made under his direction, and in conjunction with Graham and Miller, in 1851, he made a memorable report to the Secretary of State for the Home Department, on the supply of water to the metropolis (*Chem. Soc. J.*, **4**, 375). He also took part in many other important public inquiries. Of these may be mentioned that into the alleged adulteration of pale ale by strychnine, in conjunction with Graham, in 1852; the elaborate report upon original gravities, in conjunction with Graham and Redwood, published in our Journal, in 1853; and that on the subject of lighting picture galleries by gas, in conjunction with Faraday, Tyndall, Redgrave and Fowke. It was in connection with this last inquiry

that he used triethylphosphine in detecting the presence of carbon bisulphide in coal-gas.

A report which he made to De la Rue & Co. in 1858, on vegetable parchment, published at the time in the *Pharmaceutical Journal* (**18**, 273) and in *Liebig's Annalen* (**112**, 243), is historically interesting, especially as specimens are attached to the paper in the latter journal.

Experiments which he made on the changes which guttapercha undergoes under tropical influences, for the purposes of a report on this subject to the Director General of Telegraphs in India, are briefly described in a note in the Society's Journal for 1861 (p. 87).

The use of gaseous fuel in the laboratory naturally engaged his attention. The combustion furnace with perforated cylindrical clay burners which he ultimately devised is probably the most efficient yet constructed, although it suffers under the disadvantage that the temperature cannot be quickly varied, as it can be in the more modern forms of furnace in which the Bunsen burner is used.

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To pass to the consideration of Hofmann's work after he left England—full of interest and important as were many of the investigations he carried out, in comparison with that of his earlier years it may not unfairly be characterised as in a measure discursive; and it could not well be otherwise. Another opportunity such as had been afforded him at the outset of his career, and of which he had availed himself with such extraordinary success, was scarcely likely to present itself. Having determined the nature of the amines and alkaloids generally; having discovered the substituted ammoniums; in the field in which he had laboured with such perseverance, there was little left for him to do, he had so fully established the dominant properties of aminoid nitrogen.

A practically complete account of his English work is to be found in the 170 papers indexed under his name in the third volume of the Royal Society's *Catalogue of Scientific Papers*, published prior to 1864. In subsequent volumes the number is raised to 319, but these carry the record only up to the end of 1883. The volumes of the *Berichte* published after this date contain, however, only about 40 communications bearing his name.

Some of his work was based on casual, almost chance, observations; some was the outcome of opportunities such as he was always ready to avail himself of without loss of time; but the greater part naturally consisted in extending and elaborating observations made during his earlier work.

That he entered on his new career at a critical moment is clear from his own statements. Nothing shows this better than the picture

he paints in the preface to his *Introduction to Modern Chemistry*, dated March 24, 1865, in the following striking passages—

"No chemist will need to be reminded, that during the last quarter of a century the science of chemistry has undergone a profound transformation; attended, during its accomplishment, by struggles so convulsive as to represent what, in political parlance, would be appropriately termed a Revolution.

"Amid continual accessions of fact, so rapid, so voluminous, and so heterogeneous, as almost to exceed the grasp of any single mind, chemical science has been in travail, so to speak, with new laws and principles of co-ordination, engendered, perhaps, partly by the sheer force of their own deeply felt necessity, but partly, also, and mainly, due to the powerful initiative impulsion of a few philosophical master-minds.

"Based on the concurrent examination of the volumetric and ponderal combining ratios of certain typical elements, and on the recognition, in their standard combinations, of a few well marked structural types, these principles have introduced into the domain of chemistry the pregnant idea of *Classification*—the conception of a series of natural *Groups*, resembling the genera of the biological sciences, and culminating in the establishment of an orderly system, where before there had seemed to be but a chaos of disconnected facts.

"Under the influence of these and certain other cognate ideas, new views have arisen as to the constitution and chemical properties of matter; a reformed chemical notation has thence of necessity ensued; and structural relations, previously unsuspected, have disclosed identity of parentage in compounds till then deemed utterly diverse.

"It appears to be wisely ordered in scientific as in social affairs, that the innovating spirit which belongs to youth has its check and counterpoise in the conservative tendency essentially characteristic of age; so that, in the sharp collision of these rival force, new principles of any kind find a sort of fiery ordeal interposed between their first enunciation and final acceptance; doubtless the appointed test of their soundness and vitality.

"Hence the domain of chemical philosophy has, for many years past, rather resembled a tumultuous battle-plain than a field bestowed by nature for peaceful cultivation by mankind. The new ideas springing up of necessity one by one, and not always free, at their first conception, from errors and inconsistencies, have been resisted by the champions of the old chemical dogmas, as a gratuitous revolt against established authority. Controversy has naturally stimulated research, which, in its turn, has produced rapid modifications of theory; so that the aspect of chemistry has been in a state of incessant change. It is, indeed, only within the last few years that the new doctrines have acquired a logical consistency, and a consequent ascendancy throughout Europe, acquiring at length, for our long agitated science, a period of comparative calm.

"The author's lot, both as a student and as a teacher, has been cast amidst the storms of this controversial period; in which he has felt it his duty to take part on the side of innovation."

Again, in the speech which he delivered on taking his place as a

member of the Berlin Academy of Sciences in succession to E. Mitscherlich—an event which coincided with his return to Germany—he refers to the previous 25 years as a memorable period in the history of our science, during which the new discipline—the work of Liebig's creative genius—Organic Chemistry had acquired an extraordinary importance, so that

"Wo gestern kaum der Wald gelichtet war, erhob sich heute schon eine prachtvolle Stadt mit grossen Plätzen und weitauslaufenden Strassen und noch viel weiter gehendem Zukunfts-Bauplan."

He then briefly recalls the struggles which had been the natural outcome of the activity everywhere displayed by chemists in bringing new facts to light, facts which could not well be interpreted by means of the rudimentary theories inherited from mineral chemistry; and after referring to the importance which the study of volumetric relationships had acquired during the previous decade, he describes the gradual manner in which he himself became a convert to the views of the Gerhardt school. He then tells us what he regarded his mission to be at this time—

"Ob und in wie weit meine Arbeiten zur Entfaltung dieser Schule ihr Schärflein beigetragen haben, darüber erlaube ich mir kein Urtheil, wohl aber bekenne ich gern und frei, dass ich in ihren Lehren die mächtigsten Anregungen zu neuer Forschung, die willkommensten Fingerzeige für richtige Beurtheilung beobachteter Erscheinungen, endlich den einfachsten Ausdruck für die Darstellung gewonnener Resultate gefunden habe. In der That sind die Vortheile dieser Darstellungsweise so gross, die Kraft und Zeitersparniss für den Lernenden sowohl als für den Lehrer so bedeutend, dass es mir, und zwar namentlich auch in meiner neuen Stellung als Akademiker, eine Pflicht ist zur allegemeinsten Verbreitung der Anschauungen der modernen Chemie in weitestem Umfange nach besten Kräften mitzuwirken. Obwohl Fast überall anerkannt, sind doch diese Anschauungen noch sehr weit davon entfernt zu allgemeiner Geltung und namentlich zur alltäglichen Gebrauch in der Schule gekommen zu sein. Hier bliebt noch unendlich viel zu thun übrig. Die Ausbildung des neuen Systems für die Zwecke des Unterrichts ist eine Aufgabe, die bis jetzt erst sehr lückenhaft gelöst ist. In den Grenzgebieten, auf denen die Chemie anderer Disciplinen die Hand reicht, sind die Wellen der mächtigen Brandung, die sich im engeren Kreise unserer Wissenschaft selbst schon wieder zu beruhigen beginnen, nur erst gang schwach fühlbar geworden, in einigen sind diese Wellen noch gar nicht angelangt. Auch in diesem Sinne ist daher der Thätigkeit weiter Spielraum geblieben." (*Monatsbericht*, June, 1865.)

Such were Hofmann's views in 1865, but advance was to take place more rapidly than he had foreseen, and even he was to be left behind to some extent. It is a matter of common knowledge how, at this time, the undoubtedly inelastic theory of types became merged in a wider generalisation—the modern theory of structure.

Kekulé's genius gave birth to the benzene theory, our present views on valency crystallised out suddenly from the somewhat confused magma in which they had been overlooked, and a revolution was silently, almost immediately, effected—development rapidly taking place along lines already well marked out by Frankland and Kolbe, but which for a time had been obscured by the attractive simplicity of the theory of types. Hofmann, however, seems never to have thoroughly entered with full sympathy into the spirit of the new chemistry, and rarely adopted the modern style in his writings.

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His researches on colouring matters, which are a very important part of his later work, have already been so fully considered by Dr. Perkin that it will not be necessary again to refer to them here.

The first investigation of which an account was published after his return to Germany dealt with a class of diamines till then almost unknown but which have since acquired considerable importance, the so-called *amidines* (*Monatsber. Akad., Berlin*, 1865, 649; *Proc. Roy. Soc.*, 1867, 55). It was the outcome of a chance observation. A quantity of acetanilide required for the study of the chloro-, bromo- and nitro-derivatives of aniline had been prepared by means of acetyl chloride, and in seeking to recover the unattacked aniline a crystalline base was discovered of the formula $CH_3{\cdot}C(NPh)NHPh$. The production of this compound was traced to the presence in the acetyl chloride of phosphorus trichloride, and to the action of this substance on acetanilide and aniline conjointly. The new base was recognised as a homologue of the formyldiphenyldiamine which he had prepared many years before from chloroform and aniline; and on substituting formanilide* for acetanilide the formyl-diamine was obtained without difficulty. Benzanilide and several other anilides were converted into similar compounds.

Hofmann did not fail to recognise that the new bases were related to the *acediamine* which Strecker had obtained from acetamide by the action of gaseous hydrogen chloride, and years afterwards, when the formation of this compound was called in question by Tawildarow, he showed that it could be prepared without difficulty by following Strecker's directions (*Ber.*, 1884, **17**, 1954).

But the paper under consideration specially deserves attention on account of the very important foot-note that occurs in it in which the systematic nomenclature for hydrocarbons and hydrocarbon radicles since so extensively used is suggested. It was here that Hofmann first proposed to adopt names indicating the number of carbon atoms

* The production of a metallic derivative on adding strong caustic soda lye to a solution of formanilide was first called attention to in this paper.

in the compound, and to terminate the names of the hydrocarbons of the paraffin series in *ane*, and those of other series in *ene*, *ine*, &c.

In accordance with this system, the bases he prepared from formanilide, acetanilide and benzanilide were termed *methenyl*, *ethenyl* and *benzenyl-diphenyldiamine* respectively.

Many similar cases of the formation of bases by dehydration have since been studied, and especially the anhydro-bases formed by the withdrawal of the elements of water from benzenoid orthamido-derivatives now constitute an important class of compounds; in most cases, however, these are not of the same type as those studied by Hofmann, inasmuch as the withdrawal of water involves the formation of a secondary ring.

In 1888 (*Ber.*, **21**, 2332), Hofmann himself showed that the formation of such cycloid anhydro-bases was not confined to benzenoid compounds, but that they could be prepared equally well from ethylene- and propylene-diamines, and even from trimethylene-diamine; for example, that diacetylethylenediamine was converted on distillation into the acetate of the anhydro-base represented by the formula $\begin{matrix} CH_2\cdot N{:}C\cdot CH_3 \\ | \qquad\quad | \\ CH_2 \text{---} NH \end{matrix}$

With the object of preparing formanilide for further experiments on the methenyl base, as it was difficult to obtain formic acid in quantity at that time, Hofmann resorted to the old method of distilling the oxalate of the amine, and in establishing the conditions which gave rise to the best yield he was led to take note of the various bye-products. On boiling the crude distillate with muriatic acid, a considerable quantity of benzonitrile was found to distil over as this was evidently derived from the formanilide, it appeared probable that the method might be made use of for the preparation of the nitriles of other acids which were either procurable with difficulty or unknown. Succeeding with toluidine, he at once passed to naphthylamine, and obtained for the first time the nitrile of naphthoic acid.

Naphthyl cyanide, the corresponding amide, the thioamide, the amine formed by reducing this last, and the acid and a number of other derivatives were fully described in two subsequent papers (*ibid.*, **16**, 300, 445). It should be mentioned that it is shown in the last of these that the thioamide is very much more easily reduced than is the nitrile.

It may be added that this work was carried out by an English assistant, our distinguished Fellow, Mr. C. O'Sullivan, who had accompanied him to Germany.

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Hofmann's activity at this period was extraordinary: at the end of the summer of 1867 he communicated to the Berlin Academy two discoveries of fundamental importance—that of a method of preparing the isonitriles homologous with hydrogen cyanide, and that of formic or methaldehyde; accounts of the discoveries were also forwarded to the Royal Society, reaching it during the recess. Their history is best related in his own words—

"The aldehyde of the methyl series is not known; all the chemical manuals say so, and for the last 20 years my students have been duly informed thereof. It will scarcely appear strange that more efforts to become acquainted with that body should not have been made, since the masterly picture which Liebig has delineated of the aldehyde *par excellence* embraced as it were the history of the whole class, and of course also of the aldehyde in question. Nevertheless, methylic alcohol deserves our attention for more than one reason. As one of the simplest terms of the monocarbon series, occupying a position intermediate between marsh gas and carbonic acid, as a link of transition connecting methylic alcohol and formic acid, as either aldehyde or acetone, according to the point of view from which we look upon it, the compound CH_2O illustrates a greater variety of relations than any one of the higher aldehydes. But in addition to the interest with which the methyl compound has thus always been invested, this substance possesses special claims upon our attention at the present moment. Our actual method of treating organic chemistry for the purposes of instruction almost involves the necessity of starting from the methyl series. The simplest of aldehydes thus acquires quite an especial importance, and all those who, like the author of this note, are engaged in teaching, cannot fail to have sadly missed a compound which is the carrier of such varied and interesting considerations.

"The desire which I have frequently felt in my lectures of developing the idea of the genus aldehyde, when speaking of the methyl compounds, has more than once induced me to attempt the preparation of methyl aldehyde, but it was only at the conclusion of my last summer course that I succeeded, to a certain extent at all events, in attaining the object of my wishes.

"A substance possessing the composition and the properties of methylic aldehyde is formed with surprising facility if a current of atmospheric air charged with the vapour of methylic alcohol be directed upon an incandescent platinum spiral (*Proc. Roy. Soc.*, September, 1867, **16**, 156)."

This passage is eminently characteristic of Hofmann's picturesque and comprehensive style, overflowing always with the sense of the importance of the subject which he is considering, whatever its nature.

Proof that methylic aldehyde was produced in the manner described* was obtained, not by the actual isolation of the substance,

* The amount produced, as Hofmann subsequently showed (*Ber.*, 1878, 11, 1685), by using a mere spiral of platinum wire, is very small—not exceeding 1 per cent. By substituting a bundle of platinum wires enclosed in a platinum tube, the

but by the preparation from the crude liquid product by the action of sulphuretted hydrogen of a crystalline compound giving numbers on analysis corresponding with the formula CH_2S.

In two later notices (*Ber.*, 1869, **2**, 152; 1870, **3**, 584) Hofmann showed that this thio-compound was identical with the substance previously prepared by Girard by the action of nascent hydrogen on carbon bisulphide, and by Husemann from methylene iodide and potassium sulphide. He also discovered that although the aldehyde is gaseous, it very readily undergoes conversion into a solid polymeride identical with the dioxymethylene previously obtained by Butlerow from methylene iodide; this substance is depolymerised when heated, the gas obtained from it being the aldehyde, but on cooling the gas, it soon returns to the solid state. The solid thio-aldehyde, however, volatilises unchanged, its vapour density agreeing with the formula $C_3H_6S_3$, corresponding to that of the thio-aldehyde prepared from ordinary aldehyde.

Butlerow had converted the "dioxymethylene" he prepared into a sugar-like substance, and when Baeyer, soon after Hofmann's discovery of the aldehyde, specially called attention to the probability that formic aldehyde was an initial product of assimilation in plants, it became an object of the greatest interest to chemists. But it was not until several years afterwards that Loew, having much improved the method of preparing the aldehyde, corroborated and extended Butlerow's observation, and established the fact that a substance of the composition of glucose was formed by the condensation of the aldehyde under the influence of alkalis. All know how Emil Fischer, in the course of his marvellous researches on the carbohydrates, eventually proved that the synthetic product consisted of equal proportions of ordinary glucose and its isomeride of equal opposite rotatory power.

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Although the discovery of the isonitriles was in a sense accidental, it well illustrates Hofmann's highly developed acumen and readiness to seize any opportunity. In describing it (*Proc. Roy. Soc.*, 1867, **16**, 144) he says—

"In a lecture, I wanted to exhibit the interesting transformation of ammonia into prussic acid by means of chloroform, which was first observed by M. Cloez, and which illustrates so well our present views on quantivalence. When the two substances alone are allowed to act upon one another, this

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amount was raised to 5 per cent.; and by distilling off methylic alcohol, and freezing out water from the residue, it was increased to 10 per cent. The method was subsequently so much improved by Loew and by Tollens, that it became possible to prepare solutions containing 30—40 per cent. of the aldehyde (*Ber.*, 1886, **19**, 2133).

reaction can be rapidly accomplished only at a high temperature, and consequently under pressure. In order to shorten the process (in one word, in order to exhibit this important reaction in a lecture experiment), I had added potash to the mixture for the purpose of fixing the newly formed prussic acid, and was delighted to find that a few seconds ebullition was sufficient to yield a considerable amount of cyanide of potassium, so as to furnish, after the addition of the two salts of iron, a large quantity of Prussian blue. On subsequently repeating the experiment with some of the derivatives of ammonia, more especially with several primary monamines, I was astonished to observe in each case a powerful reaction, giving rise to the evolution of vapours of an almost overwhelming odour, strongly recalling that of prussic acid. But few experiments were necessary for the purpose of isolating the odoriferous body. The compounds thus formed are the substances isomeric with the hydrocyanic ethers or nitriles hitherto examined."

We read further

"The facility of procuring the necessary material, as well as old predilections, suggested the phenyl series as the one to be examined in the first place."

Less than a fortnight after the account of the cyanide of phenyl was sent to the Royal Society, he forwarded a second communication in which he states

"I have followed up the study of these new bodies, which have become more and more attractive to me in proportion as I investigated their nature."

Only Hofmann could write in this way of substances having such intolerably nauseating properties, "the penetrating odour of which," to use his own words with reference to the ethyl compound, "surpasses anything that it is possible to conceive."

The investigation came at the close of the session, and was carried on during the summer, at the end of August; and even those who never knew the man and his insatiable appetite for results, can picture to themselves what must have been his anxiety to learn more of such remarkable substances when they read, with reference to the ethyl compound—

"As the substance is rather volatile, the frequently repeated fractional distillations became a most painful operation, and more than once, while I have been engaged in these experiments, my laboratory has been almost inaccessible. Thus with a temperature of 20° I have found it desirable to interrupt, for the time, the preparation in the pure state of the cyanide of ethyl, and to resume it at a more favourable season!"

But he was not to be baulked of his prey, for he continues—

"I was, nevertheless, curious to study, even now, a true homologue of cyanide of ethyl in order to compare its properties with those of cyanide of phenyl. The boiling points of the amylic compounds being within con-

venient limits, I was induced to select the amyl series as presenting the greatest chance of success."

A week later (September 7th) yet a third note on the same subject came to the Royal Society. In this Hofmann drew attention to the fact that the isocyanides are formed along with the nitriles on distilling the sulphovinates with potassium cyanide—hence the intolerable odour of the crude product, so different from the agreeable odour of the nitriles; he also pointed out that E. Meyer, many years before, had allowed the ethyl compound to pass through his hands unrecognised, as by heating silver cyanide with ethyl iodide and distilling the product he had obtained a liquid having an overwhelming odour, and yielding ethylamine on hydrolysis.

Meyer had observed that the cyanide formed a compound with the silver cyanide. This Hofmann verified in the case of the amyl isonitrile; he only succeeded in separating the amyl cyanide by subjecting the double cyanide to dry distillation. Speaking of the silver cyanide process, he remarks—

"In the latter process, many secondary products are obtained, but by a more complete study, perhaps, it may be modified so as to diminish their quantity."

Hofmann was unaware at this time that he had been anticipated in the discovery of the isocyanides by Gautier, as only a brief reference to this chemist's results had been published. By distilling the double cyanide produced by the interaction of the alcoholic iodide and silver cyanide with potassium cyanide, Gautier obtained an almost theoretical yield of the methyl and ethyl compounds; thus effecting the modification of the method which Hofmann had spoken of as necessary to diminish the amount of secondary products.

An interesting compound—half nitrile and half isonitrile—was prepared by him from amidobenzonitrile in 1868 (*Ber.*, **1**, 194).*

In a brief note published in 1870 (*Ber.*, **3**, 766), he pointed out that the compounds formed by the union of triethylphosphine with mustard oils were resolved into the isocyanide and triethylphosphine sulphide when heated under pressure.

Although little was published by him during the next 10 years having reference to this class of compounds, they continued to occupy his attention; but, as he tells us at the outset of a communication on the action of sulphuretted hydrogen on the isonitriles (*Ber.*, 1877, **12**, 1095), he had always been obliged, whenever he again engaged in such work, to soon desist, as he could not ask those who assisted him to endure for long their almost unbearable odours.

* In the paper in which this is described attention is drawn to the remarkable manner in which nitrobenzonitrile is reconverted into benzonitrile by the action of reducing agents.

He speaks also of the "wahrhaft opfermuthigen Beistand" afforded him in the course of the experiments.

The object in view in subjecting the isonitriles to the action of sulphuretted hydrogen was to obtain thioamides from which thio-acids might be prepared, especially thioformic acid. Phenyl iso-cyanide was found to be gradually acted on and converted into thioformanilide; experiments to substitute for the pure cyanide the crude product obtained on mixing chloroform, aniline and alcoholic potash were but partially successful, much methenyldiphenylamidine being also formed.

As thioformanilide dissolves in a cold dilute solution of an alkali without undergoing change, Hofmann represented it by the formula NHPh·C(SH).

On the appearance of this paper, Bernthsen pointed out that amides might be prepared by heating amidines with sulphuretted hydrogen. Hofmann, in consequence, extended his observations, and showed that acid amides were converted into corresponding thioamides by distillation with phosphorus pentasulphide (*Ber.*, 1878, **11**, 338).

As new amines came into his hands, he could rarely resist the temptation of fully exploiting their powers of affording new compounds—the mere production of which appears at all times to have given him infinite pleasure—and of preparing the corresponding isonitrile among others. Thus, in 1884 (*Ber.*, **17**, 1914), he prepared the isonitrile from the tetramethylaniline, and in the next year (*Ber.*, **18**, 1821), that from the pentamethylaniline which he obtained in the course of the investigation of the products formed on heating aniline hydrochloride with methyl alcohol. Both are described as crystalline solids: the former as possessing the frightful odour characteristic of the phenyl compound in a but slightly diminished degree; the odour of the latter—on account of its slight volatility (m. p. 168°)—as far from being so overpowering as that of the lower homologues. Both undergo change with extreme readiness when heated—the former on distillation, the latter when heated slightly above its melting point—yielding the isomeric nitriles; these latter, on the other hand, are compounds of most remarkable stability which cannot be converted into acids by any of the methods ordinarily adopted in hydrolysing nitriles.

* * * * *

Phenylic (iso)cyanate, Ph·N:CO, it will be remembered, was discovered by Hofmann in 1849 among the products of the complex action taking place on distilling melanoximide (oxalyldiphenylguanidine). In the third of his notes of researches on the poly-ammonias, communicated to the Royal Society in May 1858 (*Proc. Roy. Soc.*, **9**, 274), a more rational method of preparing this and the until then unknown,

analogous thio-compound was described, which consisted in subjecting carbanilide and sulphocarbanilide to the action of agents such as phosphoric anhydride capable of fixing aniline. The method was soon afterwards applied in the naphthyl series, at his suggestion, by Vincent Hall (*ibid.*, 1858, **9**, 365).

Ten years later, Hofmann's first communication to the Berlin Society (*Ber.*, 1868, 25) was the forerunner of a series (*Ber.*, 1868, 169, 201; 1869, 116, 452) in which improved methods of preparing the thiocyanates analogous with mustard oil were described as well as a number of interesting derivatives formed from them.

In the course of these communications he showed that the method by which he had first prepared the phenyl analogue of mustard oil, PhN:CS, was of general application—that is to say, that the mustard oils could be obtained by combining a primary monamine, NH_2R, with carbon bisulphide; then expelling sulphuretted hydrogen from the thiocarbamate, $NHR{\cdot}CS{\cdot}SNH_3R$, by heating its solution, so converting it into the thiourea, $NHR{\cdot}CS{\cdot}NHR$; and finally distilling this urea with phosphoric anhydride.

An even simpler method consisted in boiling the solution of the thiocarbamate formed from carbon bisulphide and the monamine with an equivalent proportion (not an excess) of a metallic salt such as silver nitrate or mercuric chloride, the latter being that best suited for practical use—

$$EtHN{\cdot}CS{\cdot}SNH_3Et + AgNO_3 = NEt{\cdot}CS + NH_3Et{\cdot}NO_3 + AgSH.$$

Secondary as well as primary fatty amines, but not tertiary, may thus be converted into mustard oils, a mercaptide being formed in place of the sulfhydrate when the thiocarbamate of the secondary amine is decomposed. In the case of benzenoid thiocarbamates, change at once takes place spontaneously into sulphuretted hydrogen, mustard oil and amine, and the latter then interact, forming a thiourea which is but slowly acted on by the metallic salt: hence the method is not applicable to the preparation of benzenoid mustard oils.

Yet another method by which mustard oils could be prepared, disclosed by this investigation, consisted in adding an alcoholic solution of iodine to the alcoholic solution of the thiocarbamate, *e.g.*,

$$EtHN{\cdot}CS{\cdot}SNH_3Et + I_2 = N{\cdot}Et{\cdot}CS{\cdot}NH_3Et{\cdot}I + HI + S.$$

Three of the four isomeric butyl mustard oils, crotonyl mustard oil and angelyl mustard oil were subsequently prepared by him, the two latter from bromobutylene and bromamylene respectively (*Ber.*, 1874, 508, 514; 1879, 990).

The mustard oils were shown by Hofmann to be all readily acted on by water, by alcohols and by mercaptans, the two last forming

hemithio- and thio-urethanes—ethereal salts of thiocarbamic acids—respectively.

* * * * *

Full use was soon made of the new method of preparing mustard oils. Experiments on the action of chlorine on phenyl mustard oil, carried out in his laboratory by Sell and Zierold (*Ber.*, 1874, 1228), had led to the discovery of an isocyanophenylic chloride, $C_6H_5{\cdot}NCCl_2$. It was probable that this would be more readily prepared by the action of phosphorus pentachloride. Hofmann found (*Ber.*, 1879, 1126) that although it could be produced in such a manner, what appeared from its composition to be a simple chloro-derivative was also formed; but this had none of the properties of a mustard oil, and readily exchanged its chlorine for OH, NH_2, &c.; moreover, it was not identical with any one of the mustard oils obtained from the three chloranilines.

A variety of derivatives were prepared from this compound; on reduction it afforded a substance isomeric with both phenyl mustard oil and phenyl thiocyanate (*Ber.*, 1880, 8).

The behaviour of phenyl mustard oil with other chlorides was then studied: on heating it with benzoyl chloride a very small amount of what appeared to be a phenylated mustard oil was obtained. In the course of experiments made with the object of preparing this substance in larger quantity, benzanilide was heated with sulphur. The product proved to be identical with that prepared from the mustard oil and benzoylchloride, and was soon recognised as a member of a class of orthamido-derivatives of which a number had been obtained at about that time, viz., as $C_6H_4{<}\overset{N}{S}{>}CPh$, corresponding to the compound prepared by Ladenburg from orthamidophenol and benzoyl chloride, than which, however, it was much more stable. On fusion with alkali it was resolved into amidophenylmercaptan and benzoate, and was reproduced from the former by the action of benzoylchloride (*Ber.*, 1879, 2359).

The amidophenylmercaptan produced in this manner was shown to be the ortho-compound by preparing it from orthonitrobenzenesulphonic acid.

The compound originally obtained was thus shown to have the constitution represented by the formula $C_6H_4{<}\overset{N}{S}{>}CCl$. The corresponding base was easily prepared from amidophenylmercaptan and formic acid, and a number of homologous compounds from the mercaptan and the acid chlorides (*Ber.*, 1880, 8).

Hofmann subsequently made experiments with the object of ascertaining whether the method used in preparing the phenylated com-

pound could be applied to other amides (*Ber.*, 1880, 1223). On heating formanilide with sulphur, a very small amount of the methenyl base was obtained.

Acetanilide, however, was found to behave in an altogether peculiar manner, giving rise to the "oxalyl" compound represented by the formula $C_6H_4<^{N}_{S}>C—C<^{N}_{S}>C_6H_4$.

Although no satisfactory explanation of the nature of the change could be discovered, this formula was placed beyond question by the production of the compound in a great variety of ways; *e.g.* (1) by the action of zinc on the chlorinated methenyl base, (2) by the interaction of the methenyl base and its chlorinated derivative, and (3) by the action either of oxalic acid (in presence of phosphorus trichloride), or of oxalic ether, or of cyanogen on amidophenylmercaptan. Moreover, it was shown that the compound was converted by hydrolysis into oxalic acid and amidophenylmercaptan.

The same substance was obtained on using propionanilide, but a homologous compound was formed from succinamide.

A great number of experiments were made by him, both at this time and several years afterwards (*Ber.*, 1887, 1788, 1798, 2251), in which amidophenylmercaptan was subjected to the action of a variety of substances—acids, aldehydes, &c. In almost every case derivatives of the compound $C_6H_4<^{N}_{S}>CH$ were obtained. He also extended his observations to the corresponding naphthyl compound.

Many of the substances he prepared are of considerable interest. Thus, by the action of cyanogen, keeping the latter in excess, a compound convertible by the action of the mercaptan into the remarkable oxalyl derivative above referred to was obtained which he represented by the formula $C_6H_4<^{N}_{S}>C—C<^{NH_2}_{NH}$; on hydrolysis, this gave ammonia and the acid $C_6H_4<^{N}_{S}>C\cdot COOH$. Hofmann drew attention to the compound prepared by Bladin by the interaction of orthophenylenediamine and cyanogen as being probably analogously constituted.

In the last paper of this series, the preparation of amidophenylmercaptan was fully discussed, and attention drawn to its marked unpleasant physiological action on the skin.

Hofmann did not fail to notice that the bases he had prepared from the mercaptan bore a relation to quinoline similar to that which thiophen bears to benzene, and he was not content to merely remark this, but proved that by subjecting them to a treatment similar to that adopted in preparing cyanine from quinoline, cyanine-like substances

were produced (*Ber.*, 1887, **20**, 2262). Cyanine, it is to be remembered, was at this time recognised as the product of the interaction of the amylammonium iodides of homologous quinolines; Hofmann converted both the methenyl and ethenyl thio-base into amyl iodides, and showed that neither of these gave rise to colouring matter when heated alone with alkali, but that a mixture of the two readily afforded a cyanine-like substance corresponding to cyanine in composition. As in the quinoline series, the meth- and eth-iodides gave rise to similar products. Moreover, corresponding naphthyl compounds were prepared; and he showed that not only was it possible to "cross" the naphthyl with the phenyl compounds, but also to cross these with the quinoline compound, but, strange to say, the bases obtained from amidophenol—although strictly analogous to those prepared from the mercaptan—could not be converted into colouring matters, nor could cyanines be formed with the aid of the methiodides of dimethylaniline, dimethylparatoluidine, pyridine or collidine.

Hofmann's intense desire always to carry the argument from analogy as far as it could possibly be pressed, and to garner up every result within reach, is nowhere more strikingly manifest than in the page or two in which these results are described.

Reference may be here made to another investigation in which compounds of the same type as those derived from amidophenylmercaptan were obtained by him, viz., to that on the action of iodine on thiobenzamide. As far back as 1869 he had pointed out that the interaction takes place in accordance with the equation

$$2C_6H_3{\cdot}CSNH_2 + 2I_2 = C_{14}H_{10}N_2S + S + 4HI.$$

But the nature of the product was not ascertained until 1892, when a paper by Hofmann and Gabriel was communicated to the German Chemical Society at the meeting at which the death of the former was announced (*Ber.*, **25**, 1578). The compound was shown to be represented by the formula $C_6H_5{\cdot}C\begin{matrix}N{\cdot}S\\ \|\\ N{:}C{\cdot}C_6H_5\end{matrix}$.

* * * * *

We now pass to one of the most interesting of his later investigations.

Having found a difficulty in preparing phenyl (iso)cyanate in any quantity by distilling diphenylcarbamide with phosphoric anhydride, on noticing that hemithiophenylurethane was resolved into phenyl mustard oil and alcohol by distilling it alone or with phosphoric anhydride, he was led to attempt the preparation of phenyl (iso)cyanate by a similar process from phenylurethane, a substance easily produced by acting on aniline with ethylic chlorocarbonate (*Proc. Roy. Soc.*, 1870, **19**, 108). Admirable results were obtained, and the

tolyl, xylyl and naphthylyl compounds were equally readily prepared by the method. With reference to these, it is noteworthy that he points out that not only has the xylyl compound a feeble odour, attacking the eyes but slightly, but that it is a remarkably inert substance as compared with the analogous cyanates, including even the naphthyl compound.

Hofmann was never the man to sacrifice an opportunity. Being now in the possession of a method enabling him to prepare phenyl (iso)-cyanate, he is reminded of an interesting old observation that when brought into contact with triethylphosphine it was converted into a crystalline solid, supposed at the time to be the corresponding cyanurate. On re-investigating this substance, he found, however, that it was capable of uniting with alcohol in the proportion of $C_2H_6O : 2NPh{\cdot}CO$, forming a substituted allophanic ether, and therefore inferred that it was a dicyanic derivative (*Ber.*, 1871, **4**, 246).

Finding that substituted biurets were produced by the action of amines on the dicyanate, these observations were soon followed by others on biuret and allied compounds (*ibid.*, 262).

The subject did not again occupy his attention until 1885. He then described experiments showing that no other agent besides triethylphosphine was capable of converting phenyl (iso)cyanate into the dimolecular form before referred to; on heating it with potassium acetate, he obtained the (iso)cyanurate which he had previously prepared from triphenylmelamine (*Ber.*, 1885, **18**, 764).

It will be remembered that he had originally obtained melaniline from aniline and cyanogen chloride and carbotriphenyltriamine from aniline and carbon tetrachloride; in the fifteenth of his Notes of Researches on the Polyammonias (*Proc. Roy. Soc.*, **11**, 281), describing the production of a triethylcarbotriamine from ethylic cyanurate, he refers to the simple relation which these compounds bear to the guanidine then lately obtained by Strecker. His interest being thus awakened in guanidine, he endeavoured unsuccessfully to prepare it from carbon tetrachloride and ammonia, but succeeded, however, when nitrotrichloromethane (chloropicrin) was substituted for the tetrachloride (*Chem. Soc. J.*, 1866, **19**, 249; *Ber.*, 1868, 145).

The study of the action of iodine on diphenylsulphocarbamide, as a means of withdrawing sulphur, subsequently led him to devise a method of general application for the preparation of guanidine derivatives, consisting in the withdrawal of sulphur from a thiourea in presence of an amine (*Ber.*, 1869, 452, 455, 600, 687; 1874, 947).

Mention may also be here made of experiments which he instituted on the action of cyanogen on triphenylguanidine with the object of elucidating the formation of a peculiar red bye-product of the action of cyanogen on aniline (*Ber.*, 1870, 764).

In the course of the experiments with thioureas last referred to, observations were made which were followed up with important consequences. On desulphurising ethylthiourea by means of lead or mercuric oxide, a crystalline base was obtained which it was at once perceived might be regarded as a triethyl-derivative of melamine, *i.e.*, "cyanuramide"; but it was soon obvious that the primary product of change was a cyanamide, and that the melamine was formed from this by polymerisation. Hofmann showed that this was the case by producing the compound both from the ethylcyanamide prepared from ethylamine and cyanogen chloride—following the directions originally given by Cahours and Cloez—and from the urea.

Triphenylmelamine was prepared, in like manner, from phenylthiourea and from phenylcyanamide (*Ber.*, 1870, **3**, 264). It was shown that on hydrolysis these bases exchange amidogen for hydroxyl, ultimately yielding cyanuric ethers.

A tetraphenylmelamine having somewhat peculiar properties (*Ber.*, 1874, **7**, 1736), which he subsequently described, is perhaps appropriately referred to here.

The ethers isomeric with the (iso)cyanic ethers studied by Wurtz had, up to this time, received but slight attention, the ethyl compound alone, prepared from cyanogen chloride and sodium ethylate, having been described by Cloez under the name of *cyanetholine*. As such ethers were to be regarded as analogous in composition to cyanamide, Hofmann and Olshausen were led to think that, like this latter, they would readily polymerise and yield compounds isomeric with the cyanuric ethers. Operating in the methyl series, although they were unable to prepare the cyanate, they obtained a crystalline product yielding cyanuric acid and methyl alcohol on hydrolysis; on distillation, this was converted into the well known (iso)cyanurate—

$$\left.\begin{matrix}(CN)_3\\(CH_3)_3\end{matrix}\right\}O_3 = \left.\begin{matrix}(CO)_3\\(CH_3)_3\end{matrix}\right\}N_3.$$

A corresponding phenyl compound was prepared from sodium phenate and gaseous cyanogen chloride.* On repeating Cloez's experiments, however, they did not succeed in preparing either the true cyanate or the cyanurate, but obtained instead two compounds intermediate between the latter and melamine, viz.,

$$(C_3N_3)\left\{\begin{matrix}NH_2\\(OC_2H_5)_2\end{matrix}\right. \text{ and } (C_3N_3)\left\{\begin{matrix}(NH_2)_2\\OC_2H_5\end{matrix}\right.$$

(*Proc. Roy. Soc.*, 1870, 493). The blank was filled up, however, and

* The use of solid cyanogen chloride was subsequently recommended (*Ber.* 1885, 765).

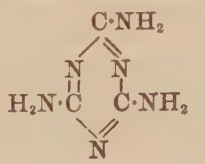
the subject much more fully investigated several years afterwards by Hofmann (*Ber.*, 1886, **19**, 2061).

Meanwhile, however, his attention had been directed to the corresponding sulphur compounds, and he had found that methylthiocyanate (prepared by distilling a mixture of potassium thiocyanate and potassium methyl sulphate) could be converted into a crystalline polymeride giving cyanuric acid and methyl mercaptan on hydrolysis (*Ber.*, 1880, **13**, 1349).

A remarkable series of further communications on this subject was published in 1885. In the first of these it is pointed out (*Ber.*, 2196) that highly purified methyl thiocyanate does not polymerise when heated, although it is partly changed into mustard oil; on adding a few drops of muriatic or sulphuric acid, however, change readily sets in. By heating the methyl thiocyanurate with sodium sulphide, he obtained thiocyanuric acid, which he also prepared from cyanuric chloride and a metallic sulphide.

By heating methyl thiocyanurate with ammonia, he obtained both the intermediate amidothioethers and also melamine; corresponding compounds were prepared with the aid of methylamine, ethylamine, dimethylamine and diethylamine. The action of various amines on cyanuric chloride was also studied very fully on this occasion (*Ber.*, 1885, **18**, 2755). A considerable number of substituted normal melamines were prepared in the course of these experiments, and naturally Hofmann was led to discuss the constitution of melamine and also of the various substituted melamines which he had previously prepared (*Ber.*, 1885, **18**, 2786).

Of the two possible formulæ,



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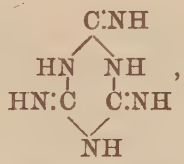

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he had no hesitation in attributing the former to melamine itself and the melamine derivatives prepared from cyanuric chloride and the thiocyanuric ethers, the fact that the hexamethylmelamine obtained with the aid of dimethylamine is reconverted into this amine on hydrolysis, as he points out, leaving no room for doubt that it is so constituted. On the other hand, the (iso)melamines obtained from thioureas are to be regarded as derivatives of a different type—as imido- not amido-compounds—being convertible into isocyanuric ethers, which yield amines on hydrolysis.

After fully discussing the constitution of cyanuric acid itself, both on this and on a subsequent occasion (*Ber.*, 1886, **19**, 2084), Hofmann

maintained the opinion that it is probably the hydroxy-compound corresponding to the amido-form of melamine. As an additional argument, he brought forward the fact that, whereas the cyanuric ethers and phosphorus pentachloride interact to form cyanuric chloride, the same agent converts methylisocyanurate into a chlorinated derivative of the formula $C_3O_3N_3(CH_2Cl)_3$—a remarkable compound which he more fully described in a later paper (*Ber.*, 1886, 2084).

But Hofmann not only recognised the existence of two forms of melamines; it did not fail to strike him that mixed intermediate forms should also exist, and in a later notice, in which a number of observations on phenylated melanilines are recorded, he pointed out that an asymmetric triphenylmelaniline is actually formed in preparing triphenylisomelaniline from phenylcyanamide. Further attention was drawn to the existence of such mixed forms in 1886 (*Ber.*, 2084).

Isothiocyanurates, corresponding to the isocyanurates, formed by the polymerisation of the mustard oils, remained to be prepared—the last paper published in Hofmann's name alone in the *Berichte* (1892, 876) was a brief announcement of their discovery as well as of that of intermediate thio-compounds formed by partially displacing the oxygen of the isocyanurates by sulphur.

Hofmann, in his Faraday lecture, after recalling the work Liebig did on the cyanides and cyanates, remarks: "From the cyanates there is but one step to the *sulphocyanates*," and then proceeds to say:—

"This name will recall to every chemist here, I feel assured, one of the most interesting of the many series of substances with which the indefatigable toils of Liebig have enriched our science. It would be vain to attempt anything like an encyclopædic account of the splendid chain of compounds derived from ammonium sulphocyanate: to exemplify the features of this chapter of Liebig's work, we must be satisfied to glance rapidly at one or two groups of these bodies; and I will select for this purpose, with your permission, the bases of the melamine series and the mellonides."

The interest which the pupil displayed in the same group of compounds may have been in part inspired by contemplation of the master's work; but when we consider how Hofmann's fundamental discovery of phenyl (iso)cyanate, and of the corresponding mustard oil, was gradually elaborated in the course of years, and we contemplate "the splendid chain of compounds" to which it gave rise, we cannot but feel that the work of the pupil is full worthy of being ranged with that of the master.

* * * * *

Before leaving his work on sulphur compounds, reference may be made to the recognition of the oil of *Cochlearia officinalis* as

the mustard oil of the butyl series (*Ber.*, 1869, **2**, 102). To ascertain the nature of the butyl present, he prepared normal, iso- and secondary butyl mustard oils, and identified the natural oil with the last of these (*Ber.*, 1874, **7**, 508). It does not appear to have been noticed whether the natural oil is optically active as it should be.

Being struck by the remarkable resemblance of the odour of benzyl mustard oil (*Ber.*, 1868, **1**, 201) to that of watercress, Hofmann examined the oil from this and a number of other plants having similar odours. He arrived at the surprising result that the oils from *Tropæolum majus* and *Lepidium sativum* (garden cress) consist of alphatoluic nitrile, $C_6H_5 \cdot CH_2 \cdot CN$, and that of *Nasturtium officinale* (watercress) of the homologous phenylpropionic nitrile (*Ber.*, 1874, **7**, 518, 520, 1293).

A very remarkable sulphur compound of the colour of potassium bichromate, formed on mixing an alcoholic solution of strychnine with a solution of yellow ammonium sulphide, was accidentally discovered by Hofmann in 1868; he at first thought that this was a compound of strychnine with a persulphide of hydrogen of the formula H_2S_3, but on subsequently examining it (*Ber.*, 1877, 1087) he came to the conclusion that its composition was represented by the formula $(C_{21}H_{22}N_2O_2)_2 \cdot H_2S_6$.

* * * * *

An investigation which led to results of considerable practical importance was that on the action of bromine on amides, of which Hofmann published particulars in 1881 (*Ber.*, 2725) and 1882 (*Ber.*, 407, 752, 762).

The first product was shown to be an addition compound convertible by the action of alkali into a monobromamide, *e.g.*, acetylmonobromamide, $CH_3 \cdot CO \cdot NHBr$, in the case of acetamide. When subjected to the further action of alkali, the bromamide is converted into carbon dioxide, hydrogen bromide and the amine of the hydrocarbon radicle of the acid from which the amide is derived, thus

$$CH_3 \cdot CO \cdot NHBr + H_2O = HBr + CO_2 + CH_3 \cdot NH_2.$$

The amine, however, is but the end product, the amide being first converted into the cyanate, $CH_3 \cdot CO \cdot NHBr = HBr + CO \cdot NCH_3$. Consequently, when a mixture of two molecular proportions of acetamide with one of bromine is acted on by alkali, methylacetylurea is formed by the union of the cyanate with the excess of acetamide.

Hofmann prepared the whole series of amines up to nonylamine, as well as heptadecylamine (from stearic acid). Many interesting details with regard to the behaviour of the various amides and the products obtained from them—including a number of urea and cyanuric derivatives—will be found in the original papers; a discussion

of the best methods of preparing the amides was published at the close of the inquiry (*Ber.*, 1882, **15**, 977).

The method appears to be of general application in all cases in which it is desired to withdraw carboxyl from an acid and displace it by amidogen, being the reverse of the method, also introduced by Hofmann, of converting an amine into the nitrile containing another atom of carbon by distilling its oxalate. It has already been made use of successfully in a number of cases in dealing with acids of unknown constitution. Instances in which the method is used with but partial success were described by Hofmann in 1885 (*Ber.*, 2734).

It remains to be mentioned that he also showed that the amines are themselves attacked by alkaline bromine solutions, being converted into the corresponding nitriles, and that the yield of amine is on this account often considerably below the theoretical amount; this happens more especially in the case of the higher terms of the series, as little as 30 per cent. of the theoretically possible amount of heptylamine being obtained, although as much as about 70 per cent. of hexylamine is produced. The formation of the nitrile is due to the conversion of the primary amine into the dibromamine, which then loses two molecular proportions of hydrogen bromide, *e.g.*,

$$C_6H_{13}\cdot CH_2\cdot NBr_2 = C_6H_{13}\cdot CN + 2HBr.$$

As Hofmann aptly remarks, the operation may be regarded as a reversal of Mendius's well known process of converting the nitriles into amines (*Ber.*, 1883, 558; 1884, 1406, 1920), and, as he showed, it may be used as a method of gradually passing down just as Mendius's process has been used in passing up the series.

* * * * *

Dr. Perkin has drawn attention, in his account of Hofmann's work on colouring matters and allied subjects, to Bardy's method of preparing the methylanilines by heating aniline hydrochloride with methyl alcohol under pressure.

In studying this method, Hofmann and Martius were led to make the important discovery that when the action was allowed to take place at a high temperature, methylated homologues of aniline were also formed; in fact, by using an excess of alcohol and heating at 280—300°, they obtained a complete series of methylated derivatives up to the tetramethylated compound, $C_6H(CH_3)_4N(CH_3)_2$, (*Ber.*, 1871, **4**, 742).

We can have no doubt who wrote the account of the work, when we read

"Wir vermissen mit Schmerzen das letzte Glied dieser Reihe, die Base mit *pentamethylirter* Phenylgruppe; wir haben sie aber trotz mehrfacher Anläufe nicht bis jetzt fassen können."

But in course of time Hofmann's grief was assuaged, as he was able to show that not only the pentamethylated base but also hexamethylbenzene were among the products when the methylating process was prolonged (*Ber.*, 1872, 720; 1882, 2895; 1884, 1912; 1885, 1821). In carrying out his later researches he had at his disposition material obtained in manufacturing solid cumidine—1 : 2 : 4 : 5-amidotrimethylbenzene—on the large scale from xylidine by the process which Martius and he had discovered (*Ber.*, 1876, 1292, 1299).

In their first paper, Hofmann and Martius had dealt only with the products which were volatile with steam; in a later paper they gave an account of the non-volatile products, especially of a tertiary diamine, $C_{15}H_{14}(NMe_2)_2$ (*Ber.*, 1873, 345; and they had meanwhile examined amidoethylbenzene, in order to compare it with the products they obtained from aniline (*Ber.*, 1869, 412).

To gain an insight into the nature of the changes involved in the methylating process, Hofmann studied the behaviour of trimethylphenylammonium iodide and showed that the methyl groups "wandered" one by one into the phenyl, giving rise finally to an amidotrimethylbenzene (*Proc. Roy. Soc.*, 1872, **21**, 47) which he subsequently identified with mesidine (*Ber.*, 1875, 61). The process was found to be equally applicable to secondary and tertiary salts, and also to the production of ethyl and amyl, but not of phenyl derivatives, diphenylamine hydrochloride remaining unchanged. Tetramethylammonium iodide was also found to be unaffected.

With regard to the position which the groups take up in the benzene nucleus, it is noteworthy that whereas Hofmann obtained paratoluidine on heating methylaniline hydrochloride, the hydriodide gave a liquid toluidine—doubtless the ortho-compound; phenyltrimethylammonium iodide, it should be added, afforded two dimethyltoluidines.

Some uncertainty attaches to Hofmann's results, in so far as the origin of the various products he obtained and their genetic relationship with aniline is concerned, as later researches by Limpach (*Ber.*, 1888, **21**, 640) appear to show that the methylation follows the ordinary para-ortho-law, and that although the presence of methyl in the meta-position in no way retards the action, methyl cannot be directly introduced into a meta-position by Hofmann's method. If this be the case it would seem, therefore, that the tetramethylated compound obtained originally by Hofmann and Martius must have been derived from xylidine present in the aniline used; and that the pentamethylated compound which the former prepared from commercial cumidine—derived from a mixture of xylidines—must have had a somewhat similar origin. It is, in fact, difficult on reading Hofmann's accounts of the investigation to ascertain to what extent the technical

products used in preparing the materials he examined were definite substances.

Further evidence pointing to the same conclusion is afforded by his remarkable observation that the dimethylxylidine prepared from trimethylphenylammonium iodide—1 : 2 : 4-xylidine—combines with methyl iodide with remarkable slowness, even at 150°, and that the trimethylated base from the same source—mesidine, as well as the tetra- and penta-methylated bases prepared from solid 1 : 2 : 4 : 5-cumidine, cannot be caused to combine with the iodide. Yet Martius and he prepared methiodides from the entire series of methylated anilines they obtained in their original investigation, and inability to form methiodides cannot therefore be regarded as a property of all the higher methylated anilines.

Hofmann appears to have been of opinion that, in the first instance, the hydrogen chloride of the aniline salt gives rise to the formation of methyl chloride, which in its turn, as he expresses it, induces substitution, first in the ammonia fragment, and ultimately in the phenyl group itself, the essential character of the process being an intramolecular change in the position of the methyl groups. Subsequently, in discussing the formation of hexamethylbenzene (*Ber.*, 1880, **13**, 1729), he suggested that the aniline underwent conversion into benzene and ammonia under the influence of the methyl alcohol, which itself became methaldehyde in the process, and that the nascent benzene was acted on by the methyl chloride and methylated.

Bearing in mind that in his original investigation on the amines he had shown that the secondary and tertiary amines are readily reconverted into primary amines by heating their hydrochlorides (*Proc. Roy. Soc.*, 1860, **10**, 594), it appears doubtful whether the process is one of direct intramolecular change; it is more probable that methylation is the result of the direct addition to the hydrocarbon radicle of the aniline of the methyl chloride or iodide, or other similar compound, and the subsequent separation of hydrogen chloride or iodide under the influence of the base present. Michel, in fact, long ago advocated this explanation (*Ber.*, 1881, **14**, 2107).

* * * * *

But one series of investigations carried out by Hofmann in Berlin remains to be considered—that relating to piperidine and conine, commencing in 1879, in the course of which he devised the method of removing the nitrogen from such compounds now recognised as one of the most important means of deciphering the constitution of alkaloids.

It seems strange to read that at so recent a date the constitution of piperidine was still undetermined, and that, although recognised to

be a secondary amine, the nature of the group C_5H_{10}, combined with NH was entirely unknown; in the hope of dissecting out the constituents of this group, Hofmann strongly heated the hydrochloride of the base, but to no purpose. He then heated it with bromine, and obtained a product, $C_5H_2Br_2(OH)N$, which appeared to be a derivative of pyridine, but this, on similar treatment, gave only a dibromo-derivative (*Ber.*, 1879, **12**, 984).

Königs soon afterwards showed that piperidine and pyridine were related in the manner suspected by Hofmann, by oxidising the former with concentrated sulphuric acid and so converting it into the latter (*Ber.*, 1879, 2341); and Schotten subsequently obtained a dibromopyridine from piperidine identical with that prepared by Hofmann from pyridine (*Ber.*, 1882, **15**, 427). Finally, Hofmann himself obtained pyridine by subjecting acetpyridine to the action of bromine (*Ber.*, 1883, **16**, 586).

Turning his attention to conine, he showed that this alkaloid contained two more atoms of hydrogen than had previously been supposed (*Ber.*, 1881, **14**, 705); and at a much later date, having distilled its hydrochloride with zinc dust, in the hope of converting it into octylamine, he obtained conyrine, $C_8H_{11}N = C_8H_{17}N - 6H$, and proved that this was either propyl or isopropylpyridine, and conine the corresponding piperidine derivative, by oxidising it to picolinic or pyridine-orthocarboxylic acid. He reconverted conyrine into conine by means of hydrogen iodide. The relation of conine to pyridine, which had often been suspected, was thus placed beyond doubt (*Ber.*, 1884, **17**, 825).

Having failed to obtain any information as to the constitution of the hydrocarbon group in piperidine by means of the experiments above referred to, recalling to mind his old observations on the decomposition of the ammonium hydroxides by heat, Hofmann subjected dimethylpiperidylammonium hydroxide to distillation. The result was an entirely unexpected one, as the hydroxide was resolved into water and "dimethylpiperidine," a compound which Hofmann regarded as formed by the passage of a methyl group into the hydrocarbon radicle. However, on combining the compound thus produced with methyl iodide, and distilling the corresponding hydroxide, trimethylamine and an unsaturated hydrocarbon, C_5H_8, were obtained (*Ber.*, 1881, 494, 659).

Conine behaved in a precisely similar manner, giving "dimethylconine," and ultimately trimethylamine and conylene, C_8H_{14}, a hydrocarbon which had been prepared from nitrosoconine by Wertheimer many years before (*Ber.*, 1881, 705).

Having ascertained that conine had the formula $C_8H_{17}N$, Hofmann was led to examine *conydrine*, a substance occurring together with

conine in hemlock, as Wertheimer—who had assigned the formula $C_8H_{17}NO$ to this base—had stated that it could be converted into conine by dehydrating agents. Hofmann confirmed Wertheimer's formula for conydrine, but on subjecting this substance to the action of muriatic acid at 220°, he obtained two isomeric bases of the formula $C_8H_{15}N$—liquid α-coniceïne and solid β-coniceïne (*Ber.*, 1881, **14**, 1497; 1884, **17**, 1908). A third substance of the same composition, γ-coniceïne, was obtained on subjecting conine to the action of bromine and alkali. It was shown that α-coniceïne could also be obtained from conine, and that conydrine was convertible into conine (*Ber.*, 1882, **15**, 2313; 1885, **5**, 109).

The remarkable results arrived at in the case of piperidine and conine naturally led Hofmann to study the effect of heat on pyridine ammonium derivatives. The results were altogether different, however, from those obtained in the case of the reduced pyridines, mono-substituted hydro-bases being formed, *e.g.*, methylhydropyridine, $C_5H_5N(CH_3)H$. The substances thus produced are characterised by their unpleasant odour, resembling that of the isonitriles and mustard oils, and on this account it was suggested by him that their production might be made use of as a means of recognising pyridine bases. The action which gives rise to them is of a very complex nature, and the yield exceedingly bad; in the hope of devising a more satisfactory method of preparation, he subjected the pyridyl ammonium iodides to the action of sodium amalgam, but obtained what appear to be dipyridyl compounds.

In studying the action of bromine in presence of alkali on the amides of polybasic acids—a series of experiments which afforded only negative results—Hofmann, in conjunction with Behrmann (*Ber.*, 1884, 2681), had occasion to examine citramide and the citraminic acids, and in the course of the inquiry was led to the discovery of citrazinic acid, a pyridine derivative from which Sell and Easterfield have but recently prepared a number of derivatives of exceptional interest.

* * * * *

Everyone is acquainted with Hofmann's modification of Gay Lussac's classical method of determining vapour density by volatilising a known weight of substance and determining the volume of vapour at a known temperature and pressure. His use of the barometric vacuum for the purpose (*Ber.*, 1868, **1**, 198) has the great advantage, not only of being an exact method, but also of permitting of the determination of vapour density at temperatures considerably below the boiling point of a substance under atmospheric pressure. A variety of improvements of minor details were described by him in

1876 (*Ber.*, **9**, 1304); and other communications on the determination of vapour density, which he brought under notice in 1877 (*Ber.*, **10**, 962) and 1878 (*Ber.*, **11**, 1684), show that the subject continued to engage his attention. It should not be forgotten that in introducing his method, Hofmann also introduced the system of using the vapour from a boiling liquid to heat the tube; although not new in principle, this was a most important practical step in advance.

* * * * *

No notice of Hofmann's scientific work would be complete if reference were not made in it to the remarkable service he rendered as a teacher in the lecture room. Sir F. Abel and Dr. Perkin have both spoken of the attention he lavished on experimental illustrations, and all who have heard him lecture are aware of the remarkable enthusiasm he invariably displayed over every successful demonstration his assistant was able to perform—for he was not often allowed by his assistants to perform his own experiments, however much they were of his own devising.

But Hofmann did not merely devise new experiments—as he tells us in the preface to his *Modern Chemistry*, in endeavouring to promote, in the country of his adoption, *the great cause of chemical education*, he broke with the classical traditions of chemical teaching; and besides studying the elements in a new order, introduced an altogether new style into lecture experimenting. This was done in response to a deeply felt want, due to his conversion to "Gerhardtism;" in fact, he commences the discourse "On Lecture Illustrations" he delivered to our Society in February 1865 by saying—

"The introduction into modern chemistry of the idea of structural types, and the prominence given thereby to volumetric considerations, involve the necessity of modifying, to a certain extent, our present style of lecture illustrations. This necessity, I believe, has been felt by many teachers who have endeavoured to reflect the present aspect of chemistry in their lectures."

He gave an account, on the occasion in question, "of the volumetrical experiments on the composition of the typical hydrogen compounds" with the study of which, during the previous few years, he had been in the habit of opening his course of lectures on experimental chemistry. The well known experiments on the volumetric composition of hydrogen chloride, water, ammonia and methane were then brought under notice. The account of the lecture printed in our Journal is illustrated with figures of the volumetric apparatus now so familiar to all students of chemistry, taken from his *Introduction to Modern Chemistry, Experimental and Theoretical: Lectures delivered in the Royal College of Chemistry, London*, which was published shortly afterwards.

He delivered a second discourse on lecture experiments on an

especially auspicious occasion, on May 15, 1869, when the German Chemical Society, of which he was President, at his invitation, met in his new laboratory in Berlin, completed only a week before.* The lecture was prefaced by an account of the steps that had led to his appointment and to the building of the laboratory, commenced on May 15, 1865. In the course of this address, referring to the opening of large chemical laboratories at Berlin and Bonn, both erected under his direction, he gave utterance to the following forecast—

"Man wird sich nicht täuschen wenn man der Gründung der beiden gross-

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* The experiments brought under notice in his lecture had reference to—(1) Increase in weight during combustion; (2) Formation of ferric acid; (3) Volumetric analysis of muriatic acid and ammonia by electrolysis; (4) Condensation of hydrogen and oxygen on conversion into gaseous water; (5) Analysis of methane and ethylene; (6) Lecture eudiometer; (7) Equality of volume between oxygen and the carbon and sulphur dioxide into which it is converted; (8) Oxidation of ammonia; (9) Evolution of oxygen from nitric and sulphuric acids; (10) Flame experiments; (11) Lecture thermoscope; (12) Comparison of the volumes of different gases when subjected to the same alterations of temperature and pressure; (13) Compression of gases by mercury; (14) Liquid sulphur dioxide; (15) Production of mercury bubbles on water; (16) Local ventilation for lecture experiments (*Ber.*, 1869, 223).

Experiments on the following subjects were afterwards described in the *Berichte*—(17) Combustion phenomena (1869, 4371); (18) Inflammation of hydrogen compounds in contact with nitric acid: (19) Observation of complementary colours in transmitted and reflected light; (20) Colouring power of aniline dyes; (21) Formation of nitric acid on combustion of hydrogen in air; (22) Liquid cyanogen; (23) Alternate reduction and oxidation (1870, 658); (24) Preparation of pure phosphine; (25) Decomposition of phosphine by electric sparks (1871, 200); (26) Eudiometer with movable sparking wires; (27) Doubling of volume on conversion of carbon dioxide into monoxide by carbon (1871, 243); (28) Oxidising action of carbon; (29) Demonstration of oxidation by conversion of colourless into coloured compounds; (30) Liquid phosphine; (31) Maximum density of water; (32) Sodium press; (33) Reversed Liedenfrost experiment to show behaviour of alkali metals to water (1874, 530); (34) Volumetric equivalence of oxygen and chlorine; (35) Analysis of hydrogen chloride; (36) Formation of water on a large scale; (37) Demonstration that gases may be liquefied both by pressure and cold (1119); (38) Electrolysis of muriatic acid; (39) Volumetric phenomena attending the formation of hydrogen chloride from hydrogen and chlorine; (40) Combustion phenomena; (41) Equality of volume of carbon dioxide with that of the oxygen from which it is formed; (42) Combustion of oxygen in hydrogen; (43) Volume weight of gaseous water; (44) Volumetric relationship of liquid and gaseous water; (45) Maximum density of water; (46) Decomposition of water by sodium; (47) Alternate decomposition and formation of water; (48) Volumetric analysis of ammonia; (49) Volumetric relation of ammonia to the nitrogen it contains; (50) Liquefied gases; (51) Manufacture of sulphuric acid; (52) Demonstration of Dulong and Petits' law; (53) Equivalence of lead and zinc; (54) Reversed Leidenfrost experiment (1882, 2656).

artigen chemischen Laboratorien, welche sich in diesem Augenblicke unter den Auspicien der Königlichen Unterrichts-Ministeriums vollendet haben, eine Bedeutung beilegt, die weit über den unmittelbaren Nutzen für den Aufschwung des chemischen Unterrichts auf den betreffenden Universitäten hinausgeht. In der Bewilligung der ausserordentlichen Mittel für die Organisation der neuen Institute ist dem Einflusse der Chemie auf die Entfaltung moderner Zustände eine Anerkennung gezollt worden, welche nicht ohne Einwirkung auf die übrigen, an diesen Errungenschaften kaum weniger betheiligten Naturwissenschaften bleiben kaum. Den eben enstandenen chemischen Instituten werden sich ähnliche, mit gleicher Liberalität ausgestaltete Anstalten für die beiden anderen grossen Zweige der Naturwissenschaft, Physik und Physiologie, anreihen, denen neben der Chemie die Zukunft angehört. Schon regt es sich lebhaft in diesem Sinne. Die Vertreter aller naturwissenschaftlichen Disciplinen fühlen, dass die grossen Opfer, welche man noch eben einem einzigen Zweige der Naturwissenschaft gebracht hat früher oder später dem eigenen Fach zu Gute kommen müssen."

Events, in his own country, have abundantly justified these remarks. Of the use made of the laboratory under his direction, evidence is to be found in the pages of the *Berichte;* all know that extraordinary activity prevailed in it, and some indication of the extent to which it was used is afforded by the fact that the last communication bearing his name, published in 1892, is marked

"Aus dem I, Berliner Univ.-Laborat, No. DCCCLXXXVIII."

Although Hofmann was not the first to study the effect of electric sparks on compound gases, the form in which we have long been accustomed to make such experiments is mainly of his devising, and had its origin in a series of remarkably interesting observations which Buff and he described in a communication to our Society in 1859 (*Chem. Soc. J.*, **12**, 273). Their experiments were undertaken

"in the hope that the slow decomposition of compound gases by the long continued passage of electric sparks might be effected by the spark current of the induction coil with such rapidity and precision as to furnish a simple experimental illustration of relations with difficulty attainable by other methods. The relation of the spaces occupied respectively by a compound gas and by the sum of its gaseous constituents is but rarely capable of *synthetical* demonstration. In most cases this relation can only be exhibited by *analytical* operations which are not always compatible with the conditions of a lecture experiment. The successful application of the spark-current appeared to promise a considerable simplification of these processes. With this view we have studied the action of the current produced by a powerful Ruhmkorff coil on the more frequently occurring compound gases and on the vapours of several liquids of low boiling point. At the same time we examined the deportment of these gases and vapours under the influence of iron or platinum coils electrically incandescent, together with the effects produced by the high temperature of the electric arc."

Among the substances sparked was carbon dioxide: they observed that this was at first decomposed into carbon monoxide and oxygen, which, after a time, recombined explosively. Thirty years later, almost at the very close of his career, Hofmann was led again to pay attention to this subject by representations from others that they had not succeeded in verifying the statement. He went fully into the matter, and showed under what conditions the alternations in the phenomena could be observed (*Ber.*, 1890, **23**, 3303). Both communications are full of interest, both on account of the observations recorded in them and of the practical information they convey; it is remarkable that the ingenious method of sparking introduced by Buff and Hofmann has not been more frequently adopted by later workers.

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The foregoing is an account, in the briefest possible terms, of the scientific work accomplished by Hofmann during a period of almost 50 years—of labours ever carried on with unremitting ardour and enthusiasm, no trace of failing interest being discoverable as years roll on, the same characteristic, inspiriting freshness of style pervading each successive communication.

Much may be learnt by the reverent study of his work; and this notice has been compiled in the hope that it may, in some measure, serve students as a guide—to enable them to grasp its bearings, and to understand the intimate interconnection of its parts.

No more enduring monument of his supreme ability as an investigator could be wished for than is afforded by the records of his labours preserved to us in the various journals. And not only of his ability as an investigator—for in studying them we perforce recognise the great leader also. No ordinary man could have induced his assistants so rapidly to carry out researches of such difficulty as that on the diamines, and so repellent as well as difficult as were those on the phosphines, the isonitriles, the isocyanates and the mustard oils.

But we cease to wonder, when we learn how closely he followed each step in every investigation which was being carried out under his direction, how every detail even was familiar to him; and when we hear how all who worked with him were stirred into enthusiasm, and were made to feel that failure to produce results was regarded by him as a real personal grievance.

Hofmann, however, not only provided most of the materials for one of the chief chapters in organic chemistry—he played besides the part of the statesman, and with marvellous effect; for the great

work accomplished under his leadership by the German Chemical Society—which has coordinated the labours of chemists throughout the world in a way that has never yet been witnessed in any other branch of science—is universally recognised as largely due to his initiative, to his great organising ability, and to his personal exertions, influence and tact. We are able to take no small share of pride in his success, as he was the first to recognise that he gained his experience among us, and that he was often guided by English models.

Cosmopolitan in speech, he was cosmopolitan in sympathies. A discovery of interest once made in his English laboratory, he forthwith communicated his results not only either to us or to the Royal Society and to his former countrymen, but also to his many friends and admirers in France; and he would have been equally ready to give expression to them in several other tongues had he felt that any useful purpose was to be served. It was no mere vain wish for notoriety that led him to spread abroad the account of his successes. The interest he took in his work was so intense, that he could not but feel that others ought to be able to enjoy with him the pleasure he experienced whenever new facts of importance came to light. Hofmann's share in promoting the spirit of freemasonry among scientific workers generally was thus very great.

And his influence in industrial circles cannot well be overrated, difficult though it be to gauge its extent. Apart from the inspiration men like Perkin and Nicholson received from him, there can be no doubt that his researches on colouring matters have had a determining effect on the course of the development of the colour industry. Had it not been for the example which he set, and the persistent manner in which he investigated colour after colour, problem after problem, we should scarcely have so soon witnessed that translation of theory into practice which is the distinguishing feature of *German chemical industry* at the present day.

It would be impossible to find a more competent witness than the author of the epic—for it is nothing less—published shortly after Hofmann's death in the *Berichte*, recounting the wondrous achievements of the long succession of chemists who have brought the coal tar industry to its present high pitch of perfection; in claiming for Hofmann a principal share in its development, Carò indulges in no mere flight of poetic phantasy, and the following closing words of his recital are singularly appropriate and full of feeling—

"Dem Führer folgen wir zu dem Fabrikthor. Noch einen letzten Blick in die Gliederung des mächtigen Werkes—sein wahres Fabrikgeheimniss wurde uns offenbart!

"Vor unserm Geiste steht wieder der Baum der Deutschen Chemischen

Industrie mit seinen ragenden Aesten und Zweigen. Wie naturgemäss—denken wir—hat sich doch sein kräftiges Wachsthum vollzogen! Boden und Nahrung fand er in der Wissenschaft und das Walten der ewigen Gesetze, die jeden Erfolg im Leben bedingen, hat auch seine Entwickelung zu der gegenwärtigen Blüthe gebracht. Der Wunsch ringt sich von der Seele los Möge nie der Sturm diesen Baum entblättern, nie der Unfriede an seinem Marke nagen!

"Wir sagen dies dem Führer. Er drückt uns die Hand. 'Und so oft Sie sich dieses Baumes erinnern, so vergessen Sie nicht'—sagt er—des treuen Gärtners, der unseres Zweiges gewartet hat, seit der Zweig noch ein Reis war—fast ein halbes Jahrhundert. Denken Sie stets in Liebe und Verehrung an unsern August Wilhelm von Hofmann."

Hofmann did his best to raise up an English tree of chemical industry, and for a while it grew apace: indeed, at one time there seemed to be every chance that it would rank as an indigenous production, as seed fell and began to spring up in turn; but alas! its roots were soon struck by canker, and it ceased to flourish. No one could be brought to understand that it not only required frequent careful pruning, but also the addition continually of new grafts; it was left too much in the charge of mere uninstructed labourers, and competent foresters who could appreciate its requirements and forward its growth were considered unnecessary.

While our adopted countryman, Hofmann strove in every possible way to promote our interests. His pupils established the new industry, which he did his utmost to support and forward when its importance once became manifest; but the circle within which favourable conditions prevailed was hopelessly narrow. We, in fact, denied him the opportunity he eagerly seized upon when it was offered to him by his own countrymen: and among them he found both *Boden und Nahrung*, for they had been properly tutored by their universities, and were prepared to accept his advice and *apply theory to practice.* Our universities, unfortunately, long thwarted us instead of aiding us, and are still too much engaged in the blind worship of the unpractical. True culture has been neglected. The struggle for scholarships and distinctions has exercised an over-mastering influence; precious years which should be spent in learning to *work* and to appreciate and apply theory have been sacrificed in committing facts to memory for the mere purpose of retailing them in examination halls—nay, worse, in sterilising and cramping minds which under a free system might develop into utmost usefulness. A change is indeed gradually coming about, but all too slowly, as—worst of all—no true public feeling on the question exists. Our schools have done their work so badly that the general public cannot properly discuss such questions, and take no interest in them.

The records of our Society show what English chemists can accom-

plish, and if the demand should arise there would now be no difficulty in finding and educating any number of capable men who could do all that would be required of them. But so long as employers of labour are not thoroughly imbued with the scientific spirit, and fail to fully avail themselves of the services of properly trained workers, no real progress is possible: for it is useless to manufacture goods you cannot sell to advantage, which those who ought to possess them will not buy.

Those of us who understand the position cannot but contemplate with envy, and yet with utmost admiration, proud words such as Caro utters in referring to the coal tar industry: "Kein Zweig der deutschen Technik trägt mit gleichem Rechte den Namen einer nationalen Industrie." It were time, however, that some sense of shame pervaded our men of business, and that the nation were brought to understand how opportunities once ours have been sacrificed, not even blindly, but in face of constant warnings; that not only the coal tar industry, but all industries in which chemistry can and should play the leading part, with few exceptions, have failed to advance during the past five and twenty years.

To quote the words used by the Council of the Royal College of Chemistry in their second report in 1848—"Capital, which has been the boast of this country, can do much, but capital directed by the lights of science may accomplish much more; and those nations who neglect to call in its aid, will, to use the prophetic words of the venerable *Humboldt*, infallibly see their prosperity diminish in proportion as neighbouring countries become strengthened and invigorated under the general influence of arts and science." It were time that the value of the legacy Hofmann has left were appraised by us—that some notice were taken of the warning which at the outset of his English career he brought under our notice.

A writer in a recent number of the *North American Review* maintains the thesis that chemistry underlies the manufacturing arts, and that hence the industrial status of a nation may be fairly estimated by the condition of its chemical knowledge.

"It is fair to hold that the country that has the best chemists will in the long run be the most prosperous and the most powerful. It will have at the lowest cost the best food, the best manufactured materials, the fewest wastes and unutilised forms of matters, the best guns, the strongest explosives, the most resistant armour. Its inhabitants will make the best use of their country's resources; they will be the most healthy, the most free from disease; they will oppose the least resistance to favourable evolution; they will be the most thrifty and the least dependent on other nations. The education of its people in chemistry and the physical sciences is the most paying investment that a country can make. Competition to-day between nations is essentially a competition in the science and applications of chemistry."

Hofmann consistently taught this doctrine when he came among us—but to no purpose; his countrymen were wiser and have proved its truth to demonstration, and the victories won in the fields of pure and applied chemistry are rapidly leading them to introduce scientific method into the conduct of their affairs generally.

Shall we ever decline to pay heed to one whom we always admired and whom we now venerate?

Hofmann was elected a Foreign Member of the Chemical Society on March 3rd, 1845, which is in itself proof of the esteem in which he was held within two years after the publication of his first paper.

He became an ordinary member of the Society in 1849, the record of the meeting on March 3 containing the entry "Augustus W. Hofmann was elected a Member of the Society."

Meanwhile he had already been appointed Foreign Secretary (in 1847); and he held this office until 1861, when he was elected President.

The Society became of age during his first year of office as President, and in this year also the Prince Consort died, who had taken so great an interest in his work and in the Royal College of Chemistry. In his second year of office, the Great Exhibition was held, with which his name will always be connected on account of the remarkable monograph he wrote describing the chemical exhibits.

As Vice-President he retained his position on our Council and as an ordinary member of the Society during the remainder of his life; but after leaving England he took no part in our work, and only once came to a meeting. Although he communicated several of his discoveries to the Royal Society, he did not once send a paper to us.

He delivered the Faraday lecture in 1875, selecting as his subject Liebig's work.

His last appearance among us was in 1884, when he presided at the dinner given on the 23rd of April in honour of his old pupil, Perkin.

He was elected a Fellow of the Royal Society in 1851. He received the Royal Medal in 1854, and the Copley Medal in 1875.

Hofmann died suddenly at Berlin, on May 5, 1892, in his 74th year.

Of the two portraits attached to these notices, one is from a photograph of Hofmann taken shortly before he left England, the other is from the heliogravure of the portrait now in the Berlin Gallery, painted in 1890 by Angeli, the celebrated German artist.

H. v. Helmholtz

HELMHOLTZ MEMORIAL LECTURE.

(Delivered January, 1896.)

By George Francis Fitzgerald, M.A., D.Sc., F.R.S.

"And Nature, that old nurse, took
The child upon her knee,
Saying 'Here is a story book
Thy father has written for thee.

"'Come wander with me' she said,
'In the regions yet untrod,
And read what is still unread,
In the manuscripts of God.'

"And he wandered away and away
With Nature, the dear old nurse,
Who sang to him night and day
The rhymes of the Universe."

Longfellow.

When standing in Chamounix, beneath Mont Blanc, we are no doubt impressed with its majesty, and oppressed with a sense of our insignificance; but we must remove to a greater distance if we would judge properly of the relative importance of the giant peaks around us, if we would see *the* great mountain towering above its neighbours, the heaven-supplied source of those glorious glaciers that in Chamounix seemed to spring from the lesser heights around. We are now only a little more than a year after Helmholtz's death, and hardly sufficiently removed from his times, from the immediate presence of his contemporaries, from the personal acquaintance of so many great minds, for us to judge with perfect confidence of the relative importance of the giant intellects around us. His contemporaries, no doubt, valued "gentle Shakespear, fancy's child," as they valued Ben Johnson or Marlow; but it was reserved for succeeding generations to appreciate how immeasurably this woodland warbler outstripped these in majesty of intellect. That Helmholtz has been one of the great scientific intellects of his time is already abundantly evident. We can, however, hardly judge what his exact position as a founder of the doctrine of conservation of energy, of the theory of vortex motion, of the principles of sight and hearing, is in relation to those other great scientific intellects, Faraday, Maxwell, and Hertz, who have laid on a new foundation our knowledge of the all-pervading ether, or Jenner and Pasteur, who have created a rational foundation for medical and surgical treatment, and originated the conceptions by means of which we hope some day

to learn the structure of matter, or Darwin, who has done more than any other, since Copernicus and Newton, to revolutionise man's conception of the world around him, and of his place in Nature.

It is remarkable how many great men have attributed their peculiar gifts to the peculiarities of their family life. Helmholtz seems to have considered the drudgery of school as little better than a necessary evil. What he liked, that entered into his life; what he disliked, was hardly assimilated at all. He puts it—"What a man does easily he usually does willingly." I would rather say—"What a man does willingly he usually does easily." It is the taste that creates the will to do, and that makes the hard work easy. His love for nature was satisfied by learning geometry from wooden blocks, by walks in the country with his father, by experiments with acids on his mother's linen, by making telescopes with spectacle glasses, by studying books on physics in his father's library. Thus was nursed, that impulse to dominate the actual world by acquiring an understanding of it which became the passion of his existence, and guided his whole life. Thus his real life seems to have been nourished by things quite outside his school experiences, and he seems hardly to have looked upon educational institutions as truly educational till, in the German University, he had scope for expanding in the directions for which his nature was specially fitted. Like an ivy plant in an herbaceous border, clipped here and there to suit its surroundings, it never expands freely, nor does itself justice, nor produces really healthy growth till transplanted to the neighbourhood of the wall over which its nature is specially fitted to make it grow, and where it develops into its perfect ideal. This passion to dominate nature drove young Helmholtz to attack great problems. Young men are favourably circumstanced for doing this. Many try, few succeed. Hope, enthusiasm, energy are theirs. Unencumbered by old habits of thought their minds develop new roads of attack. The development of habits is necessary for the individual, and hence for the race, but it stops development along new lines. Hence the necessity for kindly death, that new minds may grow, that mankind may improve. To young Helmholtz the then being discovered principle of the conservation of energy, seemed almost self-evident. He thought that all the scientific world was as satisfied as himself, except a few medical and biological students, whose studies had kept them out of the flow of physical science. For the sake of these he wrote a paper on the Conservation of Energy, and then it appeared that he was a pioneer. Physical science students had not grasped the generalisations they were engaged on. This young master mind was required to clear the new path, to call the attention of those engaged in removing some immediately present obstacle to the immense prospect

around them, to show them the country they had invaded, and hoist the flag of science in the conquered territory.

To Baconian England it seems strange to be told that physicists had to contend against Hegelianism in Germany. That preconceived notions of what ought to be may obscure mankind's vision of what is, in both scientific and religious circles, is what we all expect; but that what we in England would call metaphysical views of phenomena should obstruct diffusion of truth, shows a seriousness about metaphysics in Germany that it would be hard to parallel in England. Britain has produced one of the most original and brilliant metaphysicians since Plato, the great and good Bishop Berkeley; but this father of Hume, who startled Kant from his scholastic dreaming to create all modern metaphysics, has never been taken seriously by his fellow-countrymen. Metaphysics is to most of them inanity, and we consequently wonder, when we see metaphysical theories taken so seriously elsewhere as to produce effects similar to those produced here by authority or by religion.

Great problems attracted Helmholtz's attention: those of spontaneous generation and of the source of energy in muscular contractions. But after a little work on these, his duties as lecturer in Königsberg on general pathology and physiology, led him to invent the ophthalmoscope, which raised him so much in the estimation of the world and of his colleagues, that he was thenceforth able to devote his time and energies to the subjects he liked best himself, or to such as he could not get others to do for him. To his assistants and students he left the carrying out of investigations whose methods and ends were so far defined that a student or assistant could carry them out with occasional direction from headquarters, while he himself engaged in investigations that might lead to no result, and the methods of attacking which were as yet unknown. How fortunate for mankind that this great intellect had this assistance! that the endowments of German universities should be available for providing such assistance, instead of being frittered away in providing scholarships for wealthy schoolboys to bribe them to devote unwilling energies to the culture of their minds, an end that would be much better attained by the cheaper method of inflicting heavy fines or other such well deserved punishments on those who wilfully and wickedly throw away the great opportunities of improvement presented for their use. Helmholtz thus obtained time for continuous thought, time to wait for discoveries, time to prepare the ground of thought by familiarity with the problem in all its aspects, time for the evolution of all sorts and kinds of hypotheses to be rejected, one by one, till, by a process of natural selection, the teaming brain at last saw the true solution break forth like the sun from behind

the clouds that this sun has all along illuminated, and each bright spot of which had hitherto held out hopes of success. As the natural selection of animals gradually built up mankind from an undifferentiated jelly, so the conscious selection of a genius builds up the great idea from the germs of thought. Continuity and variety are in each case the conditions for rapid progress, and in the brain workshop of a Helmholtz we see the indefatigable workings of a superabundant productiveness bringing forth innumerable varieties for selection: the brain action is natural, too. To Helmholtz the results of his work are the "natural" outcome of what went before. Is there any real difference between the productions of nature and the productions of intellectual activity?

To oneself, no doubt the selection each time is for the sake of some ulterior end, for the attaining of some object, due to a final cause, but to another observer the brain action must all be explicable as due to efficient causes. These latter do not include the former, rather each makes the other possible. Can it be otherwise in that teaming creation of which we are observers, in which we only see efficient causes, for we are only observers, and not feelers of the thoughts of nature.

And which of all the children of his intellect did Helmholtz value most? Not the ophthalmoscope that took him a week to get to work, nor his investigations on the physiology of sight and hearing that took him years to work out in their innumerable details, nor those theories of chemical and electrical action that occupied his later years. No, it was his victories over mathematico-physical problems of fluid motion, vortex motion, and discontinuous motion that he seems to have looked upon as his greatest triumphs. These seem to be the problems that he speaks of as having given him such months and years of thought to find a solution of; that he attacked this way and that, and at last solved, and having solved, saw then a broad and easy path to lead others by; a path that was obvious enough when seen, but had yet eluded his grasp, till after years of devious wandering he reached the goal, and then discovered the direct route. Their very simplicity now makes it almost impossible for those who follow to see in these works the value Helmholtz attaches to them. Great and magnificently general as they are, laying as they do a possible, nay, probable, foundation for a dynamical explanation of all natural phenomena, they seem now so obvious that, like Gallileo's law of the motion of falling bodies which laid the foundations of all dynamics, they are almost taken for granted as a natural possession of the human mind. We are inclined rather to think our predecessors must have been blind not to see such obvious things than to credit the discoverers with preternatural insight.

To the Chemical Society the question of most importance is how Helmholtz's work bears on chemical theories. Unfortunately, there is very little really known about this in respect of vortex motion. Lord Kelvin has made the brilliant suggestion that atoms are vortex rings, and upon this all subsequent guesses have been founded; for our knowledge in this direction is very little better than guesses. Helmholtz had shown that vortices in a perfect liquid could neither create nor destroy one another. Once created, a vortex ring is permanent, like an atom of matter. It can go fast or slow, it can vibrate, it can enter into partnership with others or rebound from them, according to circumstances, but vortex rings cannot destroy one another. They can change in innumerable ways, can be drawn out into thin threads, or gathered up into spherical knots; but one of their properties, called their vorticity, remains indestructibly the same during all these changes. This was Helmholtz's great discovery, and is the foundation for Lord Kelvin's brilliant suggestion that atoms are vortex rings in a perfect liquid. Advances upon this suggestion have been made, though most of these advances have brought to light serious difficulties in the way of accepting the hypothesis in its primitive simplicity. Something has been done to attack the problem of a medium like a gas of thin vortex rings, and has brought to light two very serious difficulties. The more energy we give to the rings the greater is their inertia, and the slower they move. Now it is generally believed that the inertia of a body is independent of its temperature. We can be sure that the ratio of the inertia to gravitation is independent of temperature to a very high order of approximation. We may be practically certain that the mean temperature of the earth is much higher than that of the moon, and that of Jupiter than of his moons. Now, if the inertia of a body increased with its temperature but its coefficient of gravitation did not, it would lead to very serious discrepancies in the astronomical theory of the motions of the various members of the solar system. An investigation of possible small departures from constancy of coefficient of gravitation would be most interesting in connection with the question as to the effective inertia of electrons. Departures from constancy of refractive power seem to show that the drag of ether on matter is not exactly proportional to mass, and if any sensible amount of the inertia of matter is due to an ether disturbance accompanying its motion there might be a difference between the inertia of the matters constituting what are probably such differently constituted bodies as the planets. We cannot be at all so sure that both inertia and gravitation do not increase simultaneously with temperature. Very few experiments indeed have been made as to the variation of the weight of a body with tempera-

ture. It is difficult to weigh hot bodies accurately, and, in consequence, there does not seem to be any conclusive proof that the weight of a body does not change with its temperature. If it does not do so by a measurable amount the simple vortex ring theory of matter can hardly be true. As regards the velocity with which vortex rings move, the elementary dynamics of how sound is propagated by a medium like gas, in which the molecules are only for a short part of their time in collisions, acting on one another, and are for by far the greater part of their time engaged in flights between collisions, proves that the velocity of sound must be proportional to the velocity of flight. It is known that the velocity of sound increases with temperature, and so we are landed on the horns of a dilemma, either the molecules are not thin vortex rings in an otherwise simple liquid, or else when we give heat to a gas we are in some mysterious way taking more energy from it than we give to it. This latter suggestion, if it can really be worked out, would get over the other difficulty as to the variation of inertia with temperature, for the suggestion is based upon the supposition that we have to deal, not with the motion of the ring as a whole, but only of its rotational core. Some people may have rather a preference for this latter horn of the dilemma, but I certainly think that all we know of matter and the ether points to the conclusion that whatever atoms are, there is certainly a complicated structure in the space between the atoms. This is required to explain electromagnetic actions, and consequently atoms are certainly not simple thin vortex rings in an otherwise unmoving and structureless liquid. It has been shown that an intensely moving liquid could propagate disturbances somewhat like light, if there were no diffusion of the motion, and at the last meeting of the British Association we were told of a structure for that motion which would not diffuse.

In this connection, it may be worth while pointing out that as vortices move of themselves freely and independently of the density of the liquid, there is no necessity for supposing that the density of the liquid is small. In fact, the simple theory would point to the conclusion that its density may be greater than that of platinum. This would require the energy per cubic centimeter of the turbulent motion to which the propagation of light is due to be very large indeed, approaching a million of millions of Kilojoule's, *i.e.*, it would be equivalent to a million horse power for 10 hours a day for nearly a month. It has been suggested that an atom is a hole in a vortex cell ether. The suggestion is ingenious, but is hardly consistent with the separateness of atoms, their ability to combine and separate again regaining all their primitive properties. So far, no better suggestion has been made than that atoms are regions of vortex

motion, and as it seems quite possible that a vortex ring might take up a steady motion of association with a vortex cell, and in moving from place to place may carry energy proportional to the square of its rate of translation, and still more as no one knows with certainty how vortex rings would behave in a structureful medium such as the ether is, I prefer in our ignorance the horn of the dilemma, that holds that atoms are not simple thin vortex rings in an otherwise unmoving liquid.

The theory does more, however, than land us in dilemmas. There is another result of Helmholtz's work which, though it too is full of difficulties, has a sufficiently curious analogy to chemical facts to make it wonderfully possible that there is some connection between the two. When two parallel vortex threads are near one another, and are both rotating in the same direction, they can take up a steady condition of rotating round one another which is pretty stable. Three vortex threads can do the same, taking up positions at the corners of a triangle. Four, five, and six can behave likewise, but if we try to make seven vortices rotate round one another the condition becomes unstable. That there are unstable states of this kind seems certain, but there is also no doubt that any number of vortices could exist as a stable system, thick vortices being in fact collections of vortex filaments. The chemical analogy is, however, between these systems of vortices that become unstable when more than six are involved, and the chemical fact that no element has ever been required to possess more than six monovalent elements simply connected with it. Now, though the connection is undoubtedly far-fetched, and though the suggestion does not seem to explain why three or more hydrogen atoms should not be pretty fond of revolving round one another in a happy family, yet there is undoubtedly something very striking in the numerical coincidence between the number of bonds required for chemical combinations and the number of vortices that can be absorbed into a single system of this kind. Pending any other dynamical suggestion as to why chemical bonds are limited in numbers, there seems sufficient grounds from this coincidence for keeping the matter prominently in view, in hopes that further light may be thrown on these fundamental questions. The other directions in which one might look for numerical coincidences of this kind are in the finite numbers of stable positions of magnets, in the finite numbers of the regular solids, and of the possible crystalline systems. Considering the success that has attended the development of the analogies founded on the geometry of the tetrahedron in the case of carbon, it is certainly well worth while developing corresponding solid geometrical analogies in respect of other elements. Considering that a vortex ring is in many respects

an area over which sources are distributed on one side and sinks on the other, and that sources and sinks behave in some respects like positive and negative electrified points, there seems some possibility that vortices may in some respects behave like polar bodies. From what we know of nature, a kinetic analogy is always to be preferred to a statical one, being more probably *like* the truth. If it is required to connect the geometry of the tetrahedron as regards the asymmetric carbon bound molecules with the vortex ring theory of matter, we must proceed somewhat as follows. It appears at first sight as if it would not suffice to arrange the four vortex filaments that rotate with the carbon simply at four of the corners of a pentagon to make a system competent to circulate along with the carbon filament at its fifth corner. It is well known that four points in a plane cannot represent the atomic bonds of carbon. One of them must be out of the plane of the other three in order that the rotational properties of many carbon compounds may be represented. In the case of the vortex filaments a corresponding result might be obtained by supposing the attached filaments to be wound corkscrew fashion round the carbon filament. Such corkscrew filaments are, no doubt, possible, but, unless vortex filaments can cross one another, which is certainly not generally possible, no free vortex ring could be wound corkscrew wise round another. The same result might follow by supposing that there are right-handed and left-handed carbon atoms. Though such might undoubtedly exist, this seems a very improbable explanation of the rotational light phenomena in view of the possibility of changing one of these isomeric bodies into the other by a moderate rise of temperature. We must, then, conclude that the difference between the right- and left-hand distributions of filaments must be a difference of their order of distribution round the pentagon *taken in conjunction with* the circulation of filaments round one another. If we suppose four filaments, a, b, c, d, arranged in this order, when we go in the direction of circulation we can have a complementary system arranged in the order d, c, b, a, taken in the direction of circulation, and these two systems differ in the same sort of way as a right- and left-handed screw. In all these arrangements there would be a greater facility of interchange between a and b, *i.e.*, between neighbouring filaments, than between a, c or b, d, so that in addition to this right- and left-handed isomerism there would be a possible distinction between a, b, c, d and a, c, b, d. This, so far as I know, has not been observed, and would consequently throw doubt on the suggestion that this vortex analogy is founded on any real likeness. There seem also very great difficulties in extending the analogy to complicated cases, such as the benzene ring, where a carbon filament has to be partly satisfied by one bond of a complex

molecule, partly by one bond of another carbon atom, and partly by two bonds of a second carbon atom. Too little, however, is known of the possible combinations of vortex filaments to be at all sure whether six filaments, each with an attendant satellite, could not very well circulate round one another in a stable group. In this case, as in the former one, the direction of circulation would bring us the two isomeric distributions of the satellites round the system that is at present represented by the alternate double and single bonding.

There are several serious difficulties from the chemical point of view to the supposition that these combinations of thin vortex rings are really like what is actually taking place. The possibility of a permanent combination of rings has only been proved possible when the strengths of the components are equal. Now this is quite out of harmony with known chemical phenomena. Compare, for instance, the two similar bodies water and cetyl. Their chemical compositions, H·O·H and $C_{16}H_{33}$·O·H, and behaviour show that the complex system $C_{16}H_{33}$ goes in and out of combination in just the same sort of way as the simple atom H. Now a vortex ring, $C_{16}H_{33}$, consisting of thin filaments would according to theory be 65 times as strong as the simple H ring, and consequently would not behave as a whole in at all the same way as this H ring. If it is really necessary that the components of a system must be of the same strength, the consideration of the various alcohols is fatal to the theory that chemical combination is at all like this association of vortex rings. However, the proof that equality of strength is necessary in order to make this association permanent seems to me inconclusive, and so there may yet be something important in the analogy.

Another serious difficulty is as to the explanation of the enormous differences of mass of the atoms. Mercury, for instance, is 200 times as massive as hydrogen. Now, according to the hypothesis that has been proposed, the strength of the mercury ring is the same as that of the hydrogen one, and the only way in which it can have this enormous mass is by its having a radius 14 times as great. If the average volume occupied by an atom be considered as proportional to the sphere upon which the ring would lie as a great circle, it would follow that the volume of a mercury atom would be something like 2,800 times as great as that of a hydrogen atom. This does not seem at all in accordance with what we know of these bodies. This difficulty would be largely surmounted if we could adopt the proposal already mentioned of supposing that when dealing with vortex rings we have to deal with the momentum of the core of the ring, and not with that of the whole motion involved. We might, then, suppose that massive rings had thick cores with a slow rotation, so as to have the same strength but a greater momentum than the thinner rings,

even though the radius of the rings as a whole differed only slightly. The theory of nearly spherical and worm-like vortices would lead to a somewhat similar solution, but then the theory of their association into systems has not been at all fully worked out, and we cannot say whether it does or does not lead to results such as are known to hold in chemical combination.

A further difficulty from the chemical point of view is that carbon should be a diad, and only by becoming doubled upon itself in a way that has never been proved to be possible for a vortex ring can it become a tetrad. Similarly, nitrogen becomes essentially a monad, and there seems to be no explanation of N_2O_5. The suggested doubling by which carbon becomes a tetrad would produce two allotropic forms of tetrad carbon, one right-handed and the other left-handed, and there is no evidence for this. In fact the whole system of atomicity as evolved from the theory of the association of thin vortex rings is sadly at variance with that derived from the study of chemical facts.

This should induce study of other forms of vortex motion—study of thick rings and of spherical and worm vortices. There are several ways in which these latter are not subject to the same objections as thin ring vortices. They in some cases increase in velocity when energy is given to them, so that the objections depending on the velocity of sound increasing with temperature would not apply. The change of inertia with temperature would still exist. They could apparently swallow one another up, so that something analogous to chemical combination could exist, but too little is known about this to know whether the theory of their association would be less open to objection than that of thin rings. At the same time I expect much more from the investigation of the properties of a complex medium which would be capable of producing electromagnetic actions. Any suggestion as to the nature of atoms that does not explain electrolysis cannot be more than an analogy. There is some hope that a liquid full of energetic motion could explain electromagnetic actions, and a theory of electromagnetic actions depending entirely on the actions of electrons associated with atoms has been worked into it. The suggestion that electrons have an individual existence is undoubtedly tempting, but it is worth while keeping constantly in view the possibility that their constancy of quantity is connected with a constancy of structure of the ether rather than with any individual existence of each electron. This whole subject is so tentative that it is very doubtful indeed whether any real use could be made of these kinetic analogies at all comparable with the use that has been made of the statical analogy of carbon to a tetrahedron. Although kinetic analogies are certainly to be preferred to statical ones, yet

our knowledge of the mechanism involved is still so very imperfect that, as in the case of the elasticity of solids, and even of gases, we are perforce driven to think in statical analogies, and though we know that the energy is kinetic, to deal with it as if it were potential. There is therefore no sufficient reason at present for not using corresponding statical analogies to represent chemical equilibrium, even though we may be pretty sure that we are not dealing with the matter in the manner which is absolutely like what is actually taking place.

The possibility of right-handed and left-handed vortex atoms has been mentioned. There are, in addition to the doubling of the atom on itself already mentioned, two ways in which these might exist. There might, in the first place, be a sort of temporary right- or left-handedness produced by a corkscrew wave motion being propagated round the vortex. Such a vibration could hardly subsist permanently amongst the clash of molecules, but it may be worth keeping in view. There might, in the second place, be a circulation of liquid inside the vortex core either in the right- or left-hand direction round the line of motion of the vortex ring. This would be a permanent quality of each atom, one that no interactions of vortices could either produce or destroy. But it is a quality that might be a very serious one for the vortex ring itself if ever it got drawn out beyond a certain length of circumference, for it might then make the circular shape quite unstable, and the result would probably be a vortex tangle instead of a vortex ring. Such a vortex tangle, if it could be kept within bounds, might do very well for an atom and may be better than a vortex ring, but the theory of such a tangle is beyond me, and I am afraid there would be a tendency for it to spread itself throughout space instead of confining itself to one place. May be it is by just such a destruction of vortex ring atoms that the ether has been made, and it may be that from time to time in the immensity of space these tangles undo and reform the atoms, thus rebuilding the universe out of its fragments and utilising the chance, by which the laws of thermodynamics prophesy the end, to prevent this very consummation. Anyway there seems plenty of scope for speculations founded on Helmholtz's discovery of the law of vortex motion, though I fear that until some genius directs our attention aright it can give little or no help to the chemist in his investigations.

One of the most interesting matters of a physicochemical character that Helmholtz worked at was the application of thermodynamics to chemistry. The application is, as yet, very limited. Comparatively few chemical processes can be brought through a complete cycle of operations, and still fewer are completely reversible. Unless these two conditions can be shown clearly to be applicable, we can only

apply the principle of the conservation of energy to the process in making quantitative calculations, and the second law of thermodynamics can give us very little quantitative information. There is, however, one important class of cases of chemical action which is reversible and to which we can consequently apply thermodynamics, namely that of a large number of electrolytic phenomena. Helmholtz has done a good deal in this direction, but a great deal still requires to be done both experimentally and in working out all that can be deduced from the experiments. In his method of treating the subject, he introduced a certain quantity which he named the free energy. This name is rather misleading. One would naturally conclude that it was connected with the proportion of internal energy that can be transformed into work by means of an engine, and it is connected with this, but in such a roundabout way, that anybody might easily make mistakes about it. When the internal energy is described as being divisible into two parts, one of which is bound energy and the other free, one would naturally conclude that no matter what one did, one of them could never be turned into work, while the other could, and that there was some difference in the nature of the energy in the body that made this distinction of quality. Now the internal energy in the body is really homogeneous, and we cannot separate it out into parts having different qualities in this way. As a matter of fact, changes of temperature change free energy into bound energy and *vice versâ*, and free energy is the energy turned into work during isothermal changes, and is not derived wholly in general from the internal energy. In the case of a gas, for instance, there is during isothermal expansion practically no change in the internal energy while free energy is being expended on work. Hence the view that the internal energy can be divided into two parts, one bound and the other free, is a very forced view of what is really taking place. It is worth mentioning this because the name is seductive, and those who are not familiar with a subject are very liable to be misled by the seductive appearance of simplicity conferred by particular names. Of course this does not in the least detract from the value of the function itself which has been used under a variety of names by various investigators, and has proved in Helmholtz's hands a valuable means of deducing all that can be learned from measurements on electrolytic cells and from their alteration with concentration, temperature, &c. The complete determination of the thermodynamic properties of even one substance is not known. We know hardly anything about the changes of the specific heats of bodies with temperature and pressure. A few isolated attempts have been made to determine them, but in general our knowledge of the

thermodynamic functions of bodies is extremely meagre even as regards temperature and pressure, and almost *nil* as regards chemical changes of composition. This is a direction in which much more remains to be done by the co-operation of the chemist and the mathematical physicist. Many other applications of thermodynamics to chemical actions have been made since Helmholtz's time. By the use of so-called semipermeable diaphragms the process of diffusion of a salt in solution can be made reversible at least ideally. The theory of how semipermeable diaphragms act is not of much importance in these applications of thermodynamics, unless indeed they are necessarily destroyed by their own action. If this is the case they do not make the processes involved reversible, and all the thermodynamic investigations that have been founded on the supposition that they are themselves permanent and unaltered are invalid. All that is necessary for the thermodynamical theory is that a semipermeable diaphragm is possible, and the fact that actual diaphragms are by no means absolutely semipermeable is an objection no doubt to the observations founded on what they do and is a serious difficulty in comparing observation with calculation, but it is no more an objection to the calculation of what would take place if a semipermeable diaphragm is possible than the fact that even ice and air offer resistance is an objection to the prediction of what would occur if a stone were sliding over a perfectly smooth surface by calculation from the known principles of dynamics.

Very little is known about the theory of semipermeable membranes. It is generally assumed that there are no heat effects depending upon their presence, but the corresponding mistake in neglecting the heat effects that occur when currents of electricity enter and leave a liquid lead to serious errors in the theory of galvanic cells, and until the theory and practice of semipermeable membranes agree more closely than they do at present, it is worth while looking for something of this kind. They are often spoken of as if they were merely some kind of molecular sieve. They seem really much more analogous to Graham's second class of membrane which only permit the passage of gases which dissolve in the membrane, so that their behaviour is quite different from that of simple sieves like earthenware, &c., for which the laws of diffusion are so very simple. When we come to deal with really molecular magnitudes, it is impossible, however, to draw a hard and fast line between physical and chemical permeability. One molecule may be able to penetrate amongst others, not so much because it is of the right size to get between them as because it has the right shape to do so. One cannot fit a square bar properly into a round hole. This question of shape is here mentioned merely as an example of one of various

peculiarities of a molecule which may enable it to associate itself intimately with others in a way peculiar to itself. Such a peculiarity can in our ignorance only be called by the general term one of its chemical peculiarities. From the peculiarities of organic diaphragms there seems some reason to hope that we may be able to produce a set of judiciously constructed diaphragms each suited to let through molecular groups peculiar to itself and thus enlarge our means of what may be called chemical filtration. So far we seem to have attained very little farther than to be able to filter water from salts in solution.

At the same time many organic processes seem to require an actual carrying of material by currents such as we see in the living cells of plants. By such currents materials can be taken out of dilute solutions and then transported to places where they can, under new circumstances, be given up to strong solutions. Actions of this kind, of course, like the carrying of heat from low to high temperatures, require expenditure of energy. In living organisms we have many sources for this energy, and currents of the kind can easily be produced by superficial actions like the motion of camphor on water, which might continue till all the camphor was used up if clean water were constantly supplied.

In applying thermodynamics to chemical investigations there are some serious pitfalls into which investigators have fallen. In the application of the law of the conservation of energy there is great risk of assuming that the heat supplied is equivalent to the work done without bringing the system through a cycle. A very serious mistake of this kind has been recently published as a proof that osmotic pressure is proportional to the absolute temperature. This is very possibly true, although the experimental evidence is by no means for it, but rather the contrary, yet the proof given, which assumes that the heat supplied is all used in doing osmotic work, is entirely inconclusive. A complementary mistake is to neglect the external work entirely when it is small in the cases in the mind of the calculator, and to assume that the heat supplied is all spent in changing the internal energy. This may lead to very simple laws, and to ones that are approximately true in a great many cases, but a proof founded on any such neglect and which does not clearly point out the degree of approximation attained is utterly unsound. Yet a mistake of this very kind occurs within the first seven pages of a very valuable treatise on theoretical chemistry, so that it can hardly be considered unnecessary to warn others of such mistakes. Another pitfall is to neglect the necessity for operations being reversible. Theories as to explosions in guns and gas engines have been propounded and published in which this is neglected. The

operations in both these cases are not reversed in the engines considered, and so the generally applicable second law of thermodynamics cannot be applied to them accurately. A similar mistake has been made in calculating the efficiency of engines when the feed supply, *i.e.*, the return process, is worked by a separate engine. If this method were used in an air engine, it could easily be arranged to give an efficiency much greater than what is generally called the theoretically possible efficiency. In a recently published work, it is stated, in connection with a thermodynamic investigation, that one of the processes involved is the mixture of water and salt solution, an irreversible operation unless by means of a semipermeable diaphragm, which is not mentioned. There are several proofs in vogue depending on the supposed incapacity of a system to cool itself below its surroundings. These sometimes neglect the fact that for this to be impossible the operations must constitute a cycle. By evaporation, bodies cool themselves below their surroundings, and in some cases where vapour pressures of different materials are considered in two limbs of a closed vessel, this possibility is overlooked, and at the same time the possibility is overlooked of both the limbs getting coated with the same material by distillation of a small quantity from one to the other. The failure of these proofs does not of course involve the falsehood of the thing proved, but it shows how careful those who apply physical principles should be, to be quite familiar with the subject considered. It is as risky for a chemist to apply mathematics as for a mathematician to lecture to chemists: we should work in co-operation.

In the case of calculating the connection between osmotic pressure and the lowering of boiling point by supposing that the level of the solution is raised above that of the pure water by means of a semipermeable membrane, an extension of the theorem may be obtained by supposing the membrane sunk to different depths in the water when an interesting theorem connecting the osmotic pressure with the total pressure in a liquid can be deduced.

Notwithstanding all these pitfalls and mistakes, great advances have been due to the applications of thermodynamics to chemistry, at which Helmholtz worked so fruitfully.

Along lines closely allied to those of thermodynamics, there are an immense number of chemico-physical investigations waiting to be attacked. A good deal is known about the way in which variation of composition affects capillarity for instance, and from this it is possible to calculate how capillarity ought to affect chemical composition, but there is very little indeed known as to whether it behaves as it ought. There are an enormous number of similarly reciprocally related phenomena which are connected with one another in a

manner analogous to the way in which, for instance, freezing point and pressure are reciprocally related, and which demand attention. In all such work, the co-operation of chemists and mathematical physicists are eminently desirable. We cannot often expect the two to be united in one person with the energy and time at his disposal to do double work.

Helmholtz laid the foundation for considerable advances in our knowledge of electrolysis. By a very carefully conducted series of experiments he distinguished between the diffusion currents and electrolytic currents. The former seem to be the only representative of metallic conduction in an electrolyte. For the latter he verified with very great accuracy Faraday's law of electrolysis and showed that the chemical forces are balanced by electrical forces, and that so far there was no reason for doubting that the chemical forces are electrical. This was Faraday's position, and is largely justified by subsequent investigation. At the same time there seems no doubt but that chemical phenomena are much more complex than simple electrolysis as we know it. There are too many irreversible chemical actions for us to be able with certainty to co-ordinate them with simple reversible electrolysis such as Helmholtz specially studied. There are too many good reasons for being sure that other forces exist than merely electrical ones for us to be at all certain that it is only these latter which are of importance in chemical changes. We can balance gravitation by the elastic force of a spring, or by the centrifugal force of a pair of governor balls, but that can hardly *prove* conclusively that all these are of the same kind. We can balance electrical forces against chemical forces, but this does not prove conclusively that they are of the same kind. We know that gravitational forces and magnetic forces must exist between atoms, and though they *may* produce only a very small part of the effects observed, we hardly know enough about them to be perfectly certain that their effects *must* be very small. One of Helmholtz's own theories seems to prove conclusively that there are forces acting which are *not* electrical. Helmholtz worked fruitfully at a theory of electrical diffusion through fine tubes which assumes that there is a double electrical layer on the surface of contact of the liquid and solid caused by a differential attraction of the two materials for positive and negative electricites. Now *this* attraction cannot be a force varying inversely as the square of the distance, for if so, it would merely neutralise the action of the electricity it attracted. A layer of positive electricity attracting one of negative electricity would just attract enough to neutralise all force on the layer and Helmholtz in assuming that nevertheless the electric force along the tube due to the current flowing in it does act on the layer practically

assumes that the attraction of the liquid for electricity is *not* an electrical attraction but is a specific attraction of a different kind. If we assume that an attraction of this kind can exist between atoms and electricity, we can hardly be justified in denying that atoms can act on atoms in a similar way. If the law of action of these forces be a much higher power than the inverse square, almost all the work done in separating atoms might be done against electrical forces, although at the very small distances involved in atomic dimensions these other forces might be very much greater than the electrical forces at the same distances, and might control chemical combination.

A good deal of labour has been expended on investigating a theory of solids and liquids upon the hypothesis that atoms attract one another with a force varying inversely as the fourth power of their distance apart. Very interesting results have been obtained, many of them independent of the law of action. This particular law of action seems absolutely inadmissible, however, because it is one of the most interesting conclusions from the hypothesis that at one centimetre apart two atoms would have an attraction for one another due to this cause approximately equal to their gravitational attraction. Anything at all approaching this is conclusively negatived by the substantial agreement of the various experiments, some on a large scale and some on a small scale, by which the coefficient of gravitation has been determined. If this suggested attraction existed there would be no sort of agreement between the results obtained on a large and on a small scale. There seems every reason to think that in the case of atoms we are dealing with phenomena of a much more complicated nature than that of laws of force of this kind. We know almost certainly that in the first place we are dealing with forces which are anyway like electrical and magnetic ones, neither all attractive nor all repulsive, but some one and some the other. From the arrangements of the molecules in crystals, and the tetrahedron analogy of carbon, we may be practically certain that as far as we can deal with the question as a statical problem at all, we must deal with atoms as much more complicated structures than merely centres from which forces radiate uniformly in every direction. There seems every reason to think that atoms have special centres of attraction, and there is even good ground for thinking that the force emanating from each of these centres is directed, *i.e.*, is very much greater in some directions than in others. No theory of solids certainly can be satisfactory which overlooks this, and any theory of liquids which overlooks electrolysis must be rather lame.

It must always be recollected that no *statical* theory of a solid or

liquid medium is possible with electrical forces alone acting. Such a medium would be essentially unstable. Hence, so far as we can deal with solids and liquids as statical systems, we may be quite certain that other than electrical forces *must be* postulated. From our knowledge of solids, crystals especially, and from the success that has attended the tetrahedron theory of the carbon atom, it seems almost certain that provisionally, at least, we may safely assume that a very large number of the properties of molecules can be deduced from purely statical theories of their structure. Hence we may be quite sure that so far at least as we are working on these provisional lines, we must assume other forces than electrical ones, or any others varying inversely as the square of the distance. Take, for instance, the suggestion that when an electrolyte is subject to electrostatic induction the superficial induced charges are due to a layer of electrified ions upon its surfaces. If there were no forces other than electrical ones, these ions would fly off the surface like dust. The pressure of the surrounding gas would certainly not prevent this, for a gas never prevents the diffusion of atoms. Hence we must suppose that there are other than electrical forces keeping these ions attached to the liquid. Helmholtz, himself, states as a conclusion of his investigation of the action of reversible electrochemical actions. "A remarkable feature in these processes appears to me to consist in the fact that the attraction of the water to the salt to be dissolved can constitute so great a part of the chemical force acting between the oppositely propelled elements." There seems to be considerable danger that these forces may be neglected. So much advance has been made by assuming that bodies in solution behave in some important respects like the same body in the gaseous state, that there has been a serious danger of assuming that the physical conditions are at all like. The dynamical condition of molecules in solution is essentially and utterly different from that of a molecule in a gas. The essential condition for applying any known dynamical theory of gases to calculate their behaviour is that the time during which two molecules are within the sphere of one anothers' action is small compared with the time during which they are apart, and that consequently the chances of three or more molecules being in simultaneous collision is very small. It further follows that the character of one kind of collision has no influence upon the character of the immediately succeeding collision, a condition which is not, however, fulfilled in the succeeding chatters of the chattering collision of elastic solids. Now this essential condition for the application of the dynamics of a gas to molecules in solution is very far indeed from being fulfilled. A molecule is never outside the sphere of action of its neighbours. All we know of the

magnitudes of the interspaces between molecules in a liquid shows that each molecule is within the sphere of action of hundreds, probably of thousands, may be of millions, of its neighbours. It is probably jostling about with a path for its centre between its jostles about one hundredth part as great as its own diameter. If its centre moves at a rate comparable with that of a gaseous molecule, which seems probable from the fact that liquid molecules can escape through the surface into the surrounding gas, the molecule would bang about in its confined space, making nearly 10^{14} bangs per second, and these vibrations would be quite comparable with those of heat radiations, and the concomitant vibration of the atom may be a large part of the source of ordinary heat radiation of solids and liquids. In the case of a gas the external virial is large and the internal is small and negligible, in the case of a liquid it is exactly the reverse, the external virial is small and negligible, and the internal large and important. The dynamical theory of a medium composed of molecules which can only jostle about through distances about a hundredth part of their diameter, is evidently essentially different from that of one in which the molecules describe free paths thousands of times the molecular diameter.

The theory of semi-permeable diaphragms is in a very doubtful state. They are often spoken of as if they were sieves, and as if the forces between them and the substance in solution were unimportant. A consideration of the relative behaviour of the only really effective semi-permeable diaphragm known with that of the solid diaphragms shows that there are some important differences. The surface of a liquid with a non-volatile salt in solution is a perfect semi-permeable diaphragm. Water molecules can and do get through quite freely, but molecules of the solvee cannot. Now the presence of these non-volatile molecules in the surface certainly prevents the egress, but either does not prevent the ingress, or possibly facilitates the ingress of the volatile molecules. We know this, because the presence of the solvee reduces the vapour pressure. On the other hand, the whole theory of osmotic pressure assumes that the presence of the body in solution produces no effect, or the same effect on the ingress and egress of the molecules of the solvent. It is, no doubt, a most remarkable thing that osmotic pressure should be even roughly the same as what would be produced by the molecules of the body in solution if in the gaseous state, but to imply that the dynamical theory of the two is at all the same, or that the dynamical theory of a gas is in any sense an *explanation* of the law of osmotic pressures is not at all in accordance with what is generally meant by the word "explanation." These osmotic pressures are much more closely connected with Laplace's internal pressure in a liquid which is essentially

dependent on the forces between the molecules than with the pressure of a gas which is essentially almost independent of the forces between the molecules. The existing dynamical theory of a liquid shows that the molecules are kept apart by the mutual jostling of the molecules, and that the dynamical pressure of this jostling must be equivalent to the Laplacian pressure pulling them together. When we make a rough calculation we find that molecules going with velocities approaching those of gaseous molecules, and jostling about in the narrow interstices between molecules that have been already mentioned, would produce pressures comparable with those that have been calculated for the Laplacian pressure. Hence we conclude that although the dynamical conditions in the liquid are so very different from those in a gas, nevertheless, the two methods of calculating *these* internal pressures from the mutual jostlings that keep the molecules apart and from the attractive forces that keep them together lead to very much the same result, and that the velocity of motion of the centres of the jostling molecules may be of somewhat the same magnitude as that of the same material if it were in the state of a gas. It must be seen from this how the coincidence of these two ways of considering the same question is no matter of accident, but depends on the theory that it is the mutual kinetic jostling of the molecules against one another that keeps them apart. Hence we need not be surprised if the theory of osmotic pressure has a dynamical aspect from the point of view of attractions between the membrane and the water, the water and the body in solution, and the body in solution, and the membrane. There must be some dynamical reason why the solvent gets through the membrane while the body in solution does not. It must be due to what may be described as capillary forces between the solid and the molecules of the solvent. There is no sufficient reason for supposing that the membrane acts merely as a sieve. Calculations have been made, founded on the assumption that the membrane acts like a number of fine tubes of molecular dimensions, and that the capillarity of the solution differed from that of the solvent in contact with the walls of these tubes. Upon the supposition that the tubes are of molecular sizes, the observed osmotic pressures can thus be explained by possible capillary differences. That there is a direct relation between the osmotic pressure and capillarity can be shown by causing capillarity to raise a solvent so high in a fine tube that the vapour pressure at its concave upper surface is the same as that of the salt solution, when it is readily seen that this height is that producing osmotic pressure. By means of a fine mesh, that the solution does not wet, the converse experiment, is possible, namely, to have the surface of the solution so convex that the vapour pressure near it is the

same as near a flat surface of the solvent. These diaphragms, made of an ordinary porous material, with the only known perfect semi-permeable surface, namely, the surface of the liquid itself, kept by capillarity in its pores, prove the theoretical possibility of semi-permeable diaphragms in all cases where the body in solution is non-volatile, and enable us to discuss the theory of their working more satisfactorily than when dealing with semi-permeable diaphragms whose *modus operandi* is uncertain, or, at least, matter of dispute. These perfect semi-permeable diaphragms enable us to apply thermo-dynamics with confidence to calculate osmotic pressure. They enable us to calculate what is taking place at each point and to be sure that osmotic pressures thus calculated are not dependent on some unknown function of the diaphragm itself. We may, then, be pretty sure that, at least approximately, osmotic pressure is nearly equal to the vapour pressure of the solvee, because that is approximately the result deduced from observations on the vapour pressure of solutions. At the same time our attention is attracted by the dependence of the whole phenomenon on capillary phenomena. We naturally ask such questions as whether the vapour pressure near a newly made surface is the same as near an old surface. It is known that the capillarity of a newly formed surface differs in some cases from that of an old one. It is known that there are cases in which the solvee is concentrated into the superficial layer, and there are means for approximately calculating how far this is the case. One would naturally expect that the vapour pressure near this concentrated surface layer might be quite different from that near a newly formed surface layer which had not had time to concentrate the solvee into it. Which of these vapour pressures is the one from which we ought to calculate osmotic pressure?

That osmotic pressure is proportional to the numbers of active molecules is not particularly remarkable. When small changes are made, the effect is generally proportional to the amount of change. It is, however, very remarkable that the amount of osmotic pressure can be even approximately calculated from the gaseous pressure that would be produced by these same molecules if they alone occupied the *whole space* filled by the solution. The molecules have not got all this space to move about in. They can only move about in the interstices between the other molecules which we have every reason to think constitute only a very small part of the whole volume. From the rate of diffusion of a salt in solution we know that its molecules do not go about as if they passed freely through the water molecules. It is evident that the simplest theory of what would be the effect of substituting for a certain number of water molecules a certain number of other molecules must include a consideration of

their relative attractions and sizes, and the resultant change in the space available for jostling, to say nothing of such additional complications as direct chemical combination between the two. This latter seems to be *the* complicating cause in electrolytic solutions in which each of the molecular components of the salt molecule produces its separate effect. If that effect be due to pressures exerted by each component banging about independently of the other, a very moderate amount of independence of the two components on one another would enable them to bang about independently in the extremely narrow interstices within which they are confined. That they can thus independently produce pressure only lends a very moderate amount of confirmation to the theory that these ions are quite independent as pairs. Possibly the mere substitution of an inverse square law of action between the ions for some other law of action between particular points on each, would be quite sufficient to account for the independence observed. This suggestion is founded on the supposition that the action of an ionising solvent is to substitute electrical attractions for the more complex chemical attractions which act between molecules. The difficulty of gaseous thermodynamic theory is to explain how two atoms can be sufficiently firmly fixed together not to have independent motion, rather than to account for this independence. According to this suggestion, the special forces on ions would be electrical ones, and from the known instability of bodies subject to forces varying inversely as the square of the distance, we might naturally expect a continual interchange of partners to be taking place. This, of course, does not assume that there are no other forces in the liquid than electrical ones. I have already called attention to this necessary consequence of any theory that deals with molecules as even approximately statical systems. What it does assume is that in dilute solutions these other forces are so symmetrically distributed that they do not produce stable equilibrium within the liquid. The principal difficulty in explaining how sufficient interchange of partners can take place is in explaining the apparently very great independence required by such results as that the velocities of the ions are functions of themselves alone and independent of those to which they are attached. This difficulty would be largely got over by assuming that in solution the ions are quite as much attached to the elements of the solvent as to one another, because then the interchanges that take place will be almost always interchanges amongst molecules of the solvent, and only very seldom amongst the very rare molecules of the solvee. It is almost impossible to explain dynamically the supposition that *free* ions with their electrical charges are meandering about in the liquid in a condition that can be at all rightly called dissociated. The term "dissociated"

should be confined to a condition in which the components of a molecule are not connected by any chemical bonds at all. In that case they can diffuse freely and independently through porous diaphragms. Hence the possibility of this independent diffusion is the simple and necessary test of the independence of the components which can rightly be called dissociation. In an electrolyte there is *not* this independence. The component ions cannot diffuse independently through porous diaphragms. There is the acknowledged electrical force between the various oppositely charged ions, instead of their being *free* from one another. In even very dilute solutions this force is very considerable. If we assume that a negatively charged ion is exactly half way between two positively charged ones of course the forces on it are balanced, but if we suppose it as little as 1 per cent. nearer one than the other it becomes subject to a force of 400,000 volts per cm., drawing it to the nearer electron. This at once illustrates the instability of such a condition as that described by saying merely that these charged ions are moving about independently in the liquid. Without some other important actions existing at the same time such a condition is dynamically impossible, and although to consider the matter from this point of view may help us very much, because it gives us a rough and ready analogy to work on, yet there is great danger that it may stop important advances by an illusive appearance of explanation. In just this way the emissive and elastic solid theories of light and the caloric theory of heat gave apparent explanations of optical and heat phenomena which helped for a long time in advancing these sciences. But these same theories, by being upheld, *after they had been conclusively shown to be inadequate*, were great stumbling blocks in the way of further advances.

A good deal of importance has been attached, and rightly attached, to the fact, that the heat produced by the neutralisation of dilute alkalis by dilute acids is the same as that due to the combination of H and OH. This is certainly a most remarkable fact, but to concentrate attention on it, as if the statement that ions in solution are dissociated, took away all the difficulty surrounding the matter, obscures a very important question, namely, why is there then so little heat absorbed when the ions are dissociated by going into solution? It has been proposed to explain this by various suggestions which do little more than re-state the facts in some other form, and call for new properties of ions specially invented to suit the circumstances, which remind one very much of the ingeniously invented properties of light corpuscles that were, one by one, superadded in order to explain optical phenomena.

One way, that depends on a known cause, by which solvents may produce ionisation, is by diminishing electrical actions by their high

specific inductive capacity. There seems a good deal of reason for this supposition. High specific inductive capacity in a material can hardly mean anything else than that its molecules can have electrical charges easily produced on them at a considerable distance apart. A considerable distance apart, of course, means considerable, compared with the distance apart of charges on molecules generally, which seems to be often a very small part (about one hundredth) of the molecular diameter. This follows from considering that the work done in the combination of H and Cl may be mostly due to the attraction of electrons. It is comparatively easy to calculate at most how far apart these electrons can be in order that the known amount of work done in combination may be produced by their approach. When we do so, we find that the electrons must be jammed up quite close together. This is quite accordant with what we know of their independence from spectral observations on molecules; but it at the same time shows how very much work must be done in order to separate them to even the thickness of a molecule apart. In separating them to a hundred times their former distance one does 99 per cent. of the work that would be done in separating them altogether. Why is there not an enormous absorption of heat due to solution? The suggestion mentioned is that the presence of a body of high specific inductive capacity, like water, very much diminishes the force of attraction between the electrons by providing, what come to the same thing, as induced electrons in the water molecules to help in drawing those in the salt apart. This is an excellent suggestion; but is it not really the very same thing, under another guise, as stating that it is by chemical combination with the water that the salt has conferred upon it the property of exchanging partners? What are these electric charges supposed to be induced on the water molecules, but electrons thereon? and what is the attraction of electrons among molecules but another name for one form of chemical combination? All this hangs together, but it lends no support at all to the dynamically impossible theory that the ions are *free*. What it suggests is that this so-called freedom is due to their being in complete bondage with the solvent. That atoms or molecular groups within a molecule often can and do exchange places is quite in accordance with chemical phenomena. That they should do so of their own accord *when the molecules are arranged in a particular way* is also quite in accord with such phenomena as crystallisation where the molecules, of their own accord, arrange themselves into the crystalline form, *if* they are first polarised by near approach to the surfaces of a crystal, but not otherwise, as is evident from the well-known phenomena of supersaturation. These crystalline forces are able not only to arrange the molecules in the solution, but to move massive crystals, and it is

an important matter for investigation whether they are simply electrical or of the more complex type of chemical action. This is perhaps the simplest example of so-called catalytic actions where change is induced by the presence of a material which itself is unchanged, and shows the extensive applicability of the general principle that chemical changes depend upon particular arrangements existing, and go on of their own accord so long as the arranging power exists. It is conceded that electrolysis and its consequences can be explained by this hypothesis, and the only outstanding phenomenon that does not obviously come under this explanation is that of why osmotic pressure is the same, or approximately the same, as the gaseous pressure of the same number of molecules and which is supposed to be "explained" by saying that the molecules in the solution are free. This so-called explanation is, however, as I have already pointed out, not a dynamical explanation at all, it is only a very far-fetched dynamical analogy. Thus this supposed advantage of the free ion theory is not only illusory but misleading.

Helmholtz has called special attention to the superficial electrical layers produced at the contact interface of different materials. He worked at it in connection with electrical endosmose. The whole subject is replete with interest. We want to know more about this attraction of matter for electricity. To suppose that this is electrical itself is illusory. It would require another force to keep on this permanent electrical charge; and, besides, in our present condition of semistatical explanation of nature, we must postulate forces that vary according to other laws than the inverse square of the distance in order to produce stability. That there are these superficial actions, which are partly electrical, is beyond doubt. That these electrical layers must produce effects on capillarity is unquestionable. That the forces between bodies in contact are affected by them must be the case. That energy is involved in producing and destroying these electrical layers must be. But, how much? Is the great question in all these cases. Is the electrical force the most important one acting? Is it the one that pulls hardest? Is it the one upon which most work is done? Is it the one that controls, for instance, the heat produced when insoluble powders are mixed with water? Are the already mentioned superficial crystalline forces that polarise a solution and cause molecules to arrange themselves upon its surface; are these mainly electrical? Conversely, are the forces that cause solution mainly electrical? The cause of solubility is very imperfectly understood. May we not hope that by following up Helmholtz's investigations of these superficial layers we may discover the causes of solution. The way seems also open for investigating the causes of other catalytic actions, and thus, possibly, of chemical action in

general, which may depend essentially on suitable arrangements of molecules. The capture of a comet by the solar system depends on a suitable arrangement of the planets. By suitably arranged approaches a set of stars may either stop the relative motion of one of their number so as to cause a resulting binary system, or may confer upon one of their number a velocity such as that of 1831. Groombridge, which, unless it meet with suitable circumstances, will peg away to infinity, as it cannot be stopped by the general attraction of those it is leaving. Two stars coming from a distance will in general recede to the same distance, but two systems of stars need not all do so. After collision there may be re-arrangements of components. Similarly, the approach of two simple systems would in general lead to these receding again into the condition from which they came, while the presence of a third system to absorb or re-arrange the energy and moment of momentum of the approaching systems might enable the last state of the systems to differ essentially from that from which they came.

The whole question of the nature and existence of these forces and their connection with electrical forces, is of the very greatest interest. We may hope that ultimately all forces may be explicable by a kinetic theory of nature, but, so long as no satisfactory theory of the ether exists that explains the very simple electro-magnetic laws, we can hardly expect anything more than rough analogies in explanation, or rather illustration, of other causes for these more complex chemic actions. The actions of a medium, like a perfect liquid in intense vortical motion, are capable of illustrating these actions. In the first place, there are possible actions such as those of one vortex on another which are not propagated from place to place, but are due to every vortex, in a sense, occupying all space, and each acting on the other simultaneously everywhere. Each changes the other by a simultaneous action everywhere; there is in such actions no question of propagation. Such actions in a liquid seem to best illustrate gravitation. It is not pretended, of course, that any theory of the nature of the turbulent motion or of matter has yet been invented which would lead to the known laws of gravitation. All that is suggested is that in some action of this kind we may look for an explanation of gravitation, and that in the meanwhile these actions in a liquid are a rough illustration of how actions may exist for which we have no evidence of any propagation. A second class of action of a turbulent liquid is that due to different kinds of polarisation of its motion. Such, for instance, as that vortex filaments are concentrated in various places, or move through the liquid in various directions. There is every reason for believing that such actions would be propagated from place to place with a velocity

depending on the energy per unit volume of the turbulency of the liquid Such actions, due to polarisation of the motion in bulk, can be made to illustrate electro-magnetic actions in a wonderfully satisfactory way. Besides these two, there are the possible movements of such things as vortex rings, vortex spheres, and, in general, closed vortices, through the medium. These illustrate for us matter with its molecular structure. But besides these two, there are effects that may be due to the crinkling and waving of individual vortex filaments, to their being distorted from their circular shape of section. It is such action as this that may be expected to illustrate the chemic forces, and to which one would naturally look for an explanation of these actions, more complicated than simple electro-magnetic action. The question naturally arises, "Can these actions be propagated?" To judge from the analogy, there seems every reason to expect that they could. When we look round for any evidence of propagation of actions other than the already known sound and light vibrations, we find mysterious velocities of propagation of earthquake waves and some chemical actions on sensitive silver salts that have not yet been explained by known material or electro-magnetic laws. These may, of course, be explicable by a combination of known material and electro-magnetic action. Ether waves, of lengths comparable with a millimeter, may act on molecular groups that are much smaller than the length of the wave in a somewhat similar way to that in which light waves act on the atoms whose diameter is very much less than the lengths of the waves. Vibrations of sound frequencies seem capable of helping molecules of iron to set under magnetic force. Long ether waves alter the structure of a metallic powder; may we not expect some of the enormous range between sound and light to disturb chemical equilibrium. Besides the direct propagation of light through matter, there may be electro-magnetic actions propagated by the joint action of matter and ether. There is evidence of this in the propagation of cathode rays through solid partitions, and an investigation of this and similar cases will, it is hoped, decide whether these actions are due to the interaction of matter and ether under known electro-magnetic laws, or whether we are in presence of a propagation of energy by means of those underlying properties of the ether that seem required to explain fully what we know of chemical actions, and which might be called the chemical properties of the ether.

As we then follow out the directions pointed out by Helmholtz's work, we cannot help being impressed with how far ultimate explanations of nature lead us closer and closer to the conclusion that these phenomena of our consciousness are all explicable as differences of motion. It is the motion which is imposed upon us. Is there not,

then, reason in the suggestion that colour and sound, nay, space, time, and substance are functions of our consciousness, produced by it under the action of what may be called an external stimulus, and that the only part of the phenomenon which essentially corresponds to that stimulus is the always pervading motion. And what is the inner aspect of motion? In the only place where we can hope to answer this question, in our brains, thought is the internal aspect of motion. Is it not reasonable to hold, with the great and good Bishop Berkeley, that thought underlies all motion. A purely rational machine might get on very well through the world without believing that other brains than his own had underlying thoughts. It is the position of the consistent positivist. To him nature is what others would call a consistent dream. Such a position posits nothing that is not positively felt. It is consistent, but inhuman. For human life we require sympathy and affection. For the highest life we require the highest ideal of the Universe to work in. Can any higher exist than that, as language is a motion expressing to others our thoughts, so Nature is a language expressing thoughts, if we learn but to read them. May we not hope that studies of physiological actions, of chemical constitution and change, of vortex motion, of the laws of matter and ether, may some day enable us to discover the motions in our brains underlying sound and light, and smell and touch, and pain and pleasure, hate and love. And may we not hope, then, to be able to form some dim analogies by which we may divine what underlies the much more complex motions of organic nature as a whole, and have a scientific basis for investigating what underlies the whole sequence of organic evolution.

And Helmholtz, by his physiological researches, by his chemical researches, by his physical researches, by his mathematical researches in fluid motion, has advanced mankind by a measurable amount in the road to this splendid goal. By his physiological researches we are measurably nearer a knowledge of the mechanism by which brain motions are affected. By his physical researches we are measurably nearer a knowledge of how to apply the doctrine of the conservation of energy and thermodynamics to discover a dynamical explanation of physical processes. By his chemical researches we are measurably nearer a knowledge of how to apply these same doctrines and electromagnetism to investigate the complex problems of chemical change. By his mathematical researches on fluid motion we are measurably nearer a knowledge of that simplest form of motion in which the postulated properties are so few that it seems almost the only direction in which we can hope for a really ultimate dynamical explanation of Nature.

And Helmholtz has gone from us. Let us venerate his name.

Mit kameradschaftlichem Gruß
Ihr ergebener
Lothar Meyer

LOTHAR MEYER MEMORIAL LECTURE.

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We meet this evening at the invitation of the Council of this Society to contemplate the life and work of a man who, little more than a year ago, passed away after a sudden and painless attack, and thus would we pay our homage to the memory of one who has in so great a variety of ways contributed to the advancement of the science, the fostering and promotion of which we all have at heart.

The chronicles of the life of a man of science are usually of a simple character, presenting to all, save those who either enjoyed his personal friendship or have a special interest in the scientific work of the individual, little of apparent note. But for us, as Fellows of a Society which has lost one of its most distinguished members, and to many of whom he stood as friend and fellow student, and to the majority as guide and instructor in the fundamental theories and facts of our science, no one item of the chronicle of the life of Lothar Meyer can fail to be of interest.

Julius Lothar Meyer was born on the 19th of August, 1830, at Varel on the Jade, in the Grand Duchy of Oldenburg. His father, Dr. Friedrich August Meyer, was in practice as a medical man in that town; and his mother, Frau Anna Sophie Wilhelmine, *née* Biermann, also a native of this same place, was the daughter of a medical man who, during his lifetime, was highly respected and esteemed, and whose memory was cherished in Varel for many years after his death. Lothar Meyer's mother was an only child, the constant companion of her father, and imbibed from him a love for the profession, which enabled her not only to enter fully and sympathetically into the labours of her husband, but often—despite her feeble health—to lend assistance in surgical operations. These facts, together with the respected position which their father held, readily explain how Lothar and his brother, Professor Oskar Emil Meyer, should, at the outset of their careers, have decided to follow medicine as their life's profession. But, fortunately for science, this decision was not carried to its ultimate issue; by one brother, medicine was forsaken for chemistry, and by the other for the sister science of physics.

Lothar Meyer's early education was received at a small private school, and from thence he passed to the recently founded "Bürgerschule," in Varel, at which he remained until his fourteenth year, receiving, meanwhile, private instruction in Latin, Greek, and the modern languages. His rapid growth and consequent delicate health

necessitated the discontinuance of school work for a time, and his father placed him as a pupil under the chief gardener at the summer palace of the Grand Duke of Oldenburg, at Rastede.

The healthy occupation and the new surroundings soon served to restore the bodily health of the young Lothar, who also gained that love of nature and taste for gardening which remained a source of enjoyment and recreation to the end of his life. After a year's sojourn at Rastede, Meyer was sufficiently recovered to be able to resume his studies and to enter the Gymnasium at Oldenburg, at which school he remained until Easter of 1851, when he obtained the "*Zeugniss der Reife.*"

In the summer session of 1851, Lothar Meyer commenced the study of medicine in the University of Zürich, where Frey was Professor of Anatomy and Ludwig directed the study of Physiology. From Zürich, in 1853, he went to Würzburg, where the lectures of Virchow on Pathology appear to have been especially attractive to the then student of medicine, who threw his energies completely into the work, industriously visiting the infirmary and actively discharging his duties as a student in the practice of medicine. On the 25th of February, 1854, after a year's residence in Würzburg, Lothar Meyer graduated as Doctor of Medicine.

Notwithstanding the zeal displayed in the prosecution of his studies, ere the course was completed, doubts arose in the mind of Meyer as to the wisdom of his decision to make the practice of medicine his vocation. The attraction experienced for the more scientific side of the study gradually asserted itself, and it was only his modest estimate of his own talents which prevented him arriving at an independent decision. In his doubts as to whether he were able to advance science by his own investigations, Meyer turned to his former teacher, Professor Ludwig, asking for advice on this question. To Meyer's application the reply came with no uncertain sound, Ludwig advising Lothar Meyer to put aside all doubts, and to embrace the calling which could alone be congenial to him. The decision arrived at in the summer of 1853, to devote himself to the study of physiological chemistry, was the immediate consequence of the advice of the teacher; and in the following spring, when his medical studies had been completed and the examination for the Doctor's Degree had been passed, Lothar Meyer turned his steps to Heidelberg to study chemistry under Bunsen, and to complete the working out of his dissertation. This latter occupied Meyer's energies until the autumn of 1856, by which time the investigation on the "Gases of the Blood" was published and forwarded to the Medical Faculty of Würzburg, by whom it was accepted as inaugural dissertation for the Doctor's Degree.

The years spent at Heidelberg were times of great moment, and their influence is to be distinctly traced in the subsequent work of his life. Many are there in the foremost ranks of the Fellows of this Society who, like Lothar Meyer, cherish the fondest recollection of the genial influence of their teacher, Robert Bunsen, whose reputation for so many years attracted students of chemistry from all parts of the world to Heidelberg. Wherein the attraction lay, those of us who have not been so privileged can only guess; assuredly it was not to be found in a laboratory equipped with all our modern appliances, which do so much to ease the work of a student and so little to develop his resourcefulness; but rather in the results, which cast a halo round the meagre tools with which so many of the all-important discoveries in our science have been made, and make these the desperation of our modern refinements. A description of Gmelin's laboratory in the cloisters of the old monastery at Heidelberg, in which Meyer worked for a year side by side with one of our past Presidents, Sir Henry Roscoe, who has so successfully transplanted much of the Bunsen enthusiasm and methods to this country with inestimable benefit, might serve to rouse feelings of doubt and astonishment in the minds of the present day student at the possibility of doing efficient work, where combustions were made with charcoal as fuel, and other heating operations performed with Berzelius's spirit lamp; it may, perhaps, serve to heighten their appreciation of the skill and ability of those who, by the use of such appliances, could obtain results of which we have so excellent an example in Lothar Meyer's classical investigation of the "Gases of the Blood."

During Meyer's Heidelberg "*Studienzeit*" the new laboratory was opened, with gas and water laid on to all the benches, and the spirit lamp replaced by the Bunsen burner. What these altered conditions of work meant to Meyer and his fellow students it is difficult for many of us to fully realise. The recollection of the Heidelberg days was ever a source of pleasure and delight to Meyer, who frequently referred to his "*hoch verehrter Lehrer*," to whom he dedicated what must be regarded as his *magnum opus—Die Modernen Theorien der Chemie;* nor did Meyer, in recalling the past, forget to remind his hearers of his fellow students, with many of whom he formed life-long friendships. The names of these fellow students include many whose names are honourably associated with the growth and extension of the science of Chemistry during the past 40 years, as the following list attests:—Roscoe, Russell, Atkinson, Baeyer, Beilstein, Barth, Landolt, Lieben, Meidinger, Pebal, Quincke, and Schischkow. Nor should it be forgotten that at this time there worked at Heidelberg, in the capacity of Privat-Docent, August Kekulé, to whom we owe the recognition of the tetravalency of carbon and the theoretical elucidation of the

constitution of benzene and of the aromatic compounds, theories which have so materially contributed to the advancement of organic chemistry during the past 30 years.

During the years spent at Heidelberg, the separation from medicine gradually became more pronounced, and the final step drew nearer. Whilst at the University of Heidelberg, Meyer attended Kirchhoff's lectures, and thus gained an introduction and insight into the mathematical treatment of scientific questions. The decisive blow was struck, the election made, when Lothar Meyer, in company with his friend, Pebal, and in answer to his brother's entreaty, turned his steps to Königsberg—there to devote himself to the study of mathematical physics under the direction of Professor Franz Neumann. From that moment, to quote the words of Professor Oskar Emil Meyer, "*war die Richtung entschieden, in der Lothar's Forschergeist in Zukunft thätig sein sollte, er war für die physikalische Chemie gewonnen.*"

During the year and a half spent at Königsberg Meyer prosecuted an investigation on the action of carbon monoxide on the blood, which, in the spring of 1858, was presented to the Faculty of Philosophy in Breslau as dissertation, with the title *De Sanguine Oxydo Carbonico infecto*, for which he obtained in July of the same year the degree of Doctor of Philosophy. In the February of the following year, Lothar Meyer established himself as Privat-Docent in Physics and Chemistry in the University of Breslau, presenting for this purpose a brochure on the "Chemical Teachings of Berthollet and of Berzelius," and selecting for his inaugural lecture the subject of the "so-called Volumetric Methods of Chemistry." At the outset, Meyer undertook the direction of the chemical laboratory attached to the Physiological Institution, and during his residence in Breslau, delivered several courses of lectures on various branches of chemistry applied to physiology, and conducted tutorial classes in both Inorganic and Organic Chemistry.

In Professor Seubert's account of the life and work of his highly esteemed and honoured teacher, to which, as also to the writer, I would wish to express my indebtedness for much of the information embodied in this lecture, there is reproduced a letter from the Curator of the University, Ober-Präsident von Schleinitz, which shows how completely and unselfishly Meyer threw himself into his new sphere of work; not contenting himself with unstinted devotion of time and energy, he unsparingly and liberally dispensed much of his worldly goods for the benefit of the Institute. This is all the more worthy of note, seeing that Lothar Meyer himself was not by any means a rich man, and the legacy he inherited from his father, who died a year before Meyer began his university studies, had already

been materially diminished to supply the "needful" during the "*Lehr- und Wanderjahren.*"

In the winter of 1859 one of the Heidelberg group of friends, Beilstein, whose name is a household word amongst chemists, came to Breslau in the capacity of Assistant to Professor Löwig, and in 1864 Lothar Meyer was joined by his brother, Oskar Emil Meyer, who became Professor Extraordinary in Mathematics and Mathematical Physics, to succeed in 1867 to the position of Professor, which he still occupies.

It was during the residence at Breslau that the *Modernen Theorien der Chemie* was written, as Meyer himself tells us in his preface to the fourth edition, "with the desire and hope that its publication might contribute to the removal of doubts and uncertainties, so frequently expressed at that time, as to the character of the views and theories then contending for supremacy in chemistry." "And at the same time to give to others interested in the science an account such as would lead to an understanding of the change through which the system of chemistry had just passed."

The book was written in 1862, but not published until 1864; it attracted considerable attention at the time, and has materially contributed to spread the fame of Lothar Meyer in all parts of the scientific world.

Two years after the publication of this work, Meyer received an invitation to become a teacher in the School of Forestry at Neustadt-Eberswalde, with the understanding that, should circumstances allow, he should receive a Professorship. The invitation was accepted, and in October, 1866, after seven years' activity in Breslau, Lothar Meyer began the duties of his new position. The post can scarcely be regarded as an ideal one for a specialist, and the description given in the invitation cannot be considered as altogether encouraging to one of Meyer's tendencies, as indicated by his published works. He was here required to teach the whole of inorganic natural science, more especially mineralogy, chemistry, and physics, and also to undertake the direction of the study of botany.

Before settling at Eberswalde, Meyer married on the 16th August, 1866, Johanna Volkmann, a relative of the famous surgeon, Volkmann. Frau Meyer, to whom I am indebted for directing my attention to several important facts in her husband's career, still survives, together with their four children.

The two years spent at Eberswalde do not appear to have afforded many opportunities for the development of his ability as an investigator, and Meyer cannot long have hesitated as to the manner of the reply he should make to the invitation received in February, 1868, to become the successor of Weltzein at the Carlsruhe Polytechnicum,

the duties of which Professorship he took over in the autumn of this same year.

Shortly after the settlement at Carlsruhe came an invitation to the Professorship at Königsberg in Prussia, which was declined chiefly on the grounds of geographical position and doubts as to the suitability of the climate—a decision the more readily made as the Government undertook, in accordance with the wishes expressed, to provide a residence for the Professor nearer to the Polytechnicum than the one he occupied. The necessity for the change was shown when, in the autumn of 1874, Meyer failed in health to such an extent as to necessitate him relinquishing his duties for the entire winter session, 1874—1875.

The "even tenour" of the days at Carlsruhe was also interrupted by the outbreak of hostilities between France and Germany, and the Polytechnicum was transformed into a hospital for the reception of the wounded. Reviving his medical studies, the professor of chemistry became the active and zealous surgeon. In recognition of these services, Meyer received, at the conclusion of the war, the medal for non-combatants and the "*Erinnerungs-Zeichen für Hülfsthätigkeit im Kriege.*" By these rewards for services rendered to his country in its hour of need Meyer, throughout his life, set more than special store.

During the residence in Carlsruhe, which extended over some eight years, an attachment to the place had been gradually formed, and the worth of the man had made itself felt throughout the widest circles of its life. Still the call to fill the Chair of Chemistry in the University of Tübingen, in succession to Fittig, who had been promoted to Strasburg, was one which could not be resisted, offering as it did a freer and more congenial field of labour than that afforded by the necessarily more restricted teaching of the Polytechnicum. Thus, in the spring of 1876, Lothar Meyer became university professor, and for him then began the most productive period of his life. Many investigations commenced in the earlier days and discontinued by reason of unfavourable conditions, were again resumed and brought to a final issue. The name of the Professor served to attract students to the laboratories at Tübingen, and amongst these were to be found representatives of many lands who, in Lothar Meyer, found not only the man of learning, the conscientious, painstaking and inspiring teacher, and all that his fame would entitle them to expect, but also one desirous and ready to be their friend.

His pupil, and for many years assistant and colleague, Professor Seubert, has given in the Memoir recently published by the German Chemical Society of Berlin, a sketch of the daily life at Tübingen, which shows the high ideal Lothar Meyer had formed of the duties of

his position, and with what marked success that ideal was realised. From this portrayal we carry away with us the picture of a man endowed with gifts and high intellectual powers which entitle his name to a foremost position amongst the names of those who have been contributors to the scientific development of chemistry during the past 40 years. To these were added that modesty and simplicity of character, that love of truth and high sense of honour which secured the respect and appreciation of his colleagues, and inspired the goodwill of his fellow townsmen.

The meeting of the British Association in Manchester in 1887, memorable as it was in many ways, was more than ordinarily so to chemists. The place of meeting was John Dalton's adopted city, the President, Sir Henry E. Roscoe, the founder of the School of Chemistry there, and to whose zeal and devotion Manchester is chiefly indebted for the erection of the pile of buildings in which the Association was housed, and there—further to enhance the interest—were to be seen Meyer and Mendeléeff genially active in promoting the work of Section B, under the presidency of one of Liebig's pupils, Dr. Schunck, whose investigations have greatly added to our stock of knowledge of alizarin, indigo, chlorophyll, and other vegetable colouring matters. I am reminded of one incident during the meeting which must have left an impression on the minds of all those present; when, at the conclusion of Dr. Schunck's address, there was a call for a speech from Mendeléef, he declined to make an attempt to address the section in English, and simply rose in his place to bow his acknowledgments, an action followed by the rising of Meyer from his seat next to Mendeléeff, and who, as if to prevent any misconception, prefaced his speech with the declaration, "I am not Mendeléeff," a statement which may, perhaps, have disappointed some of his hearers, but the round of applause which greeted his further remark, "I am Lothar Meyer," proved that the feeling, if it existed at all, was more than counterbalanced by the anticipation of the pleasure of listening to the words of one whose name will ever in the annals of our science be justly associated with that of the great Russian chemist. The applause which greeted this opening having subsided, Meyer, speaking in faultless English, asked permission to address the section in German, and then proceeded, on behalf of Mendeléeff and other foreign chemists present, to express the pleasure they had derived from listening to the Presidential address.

For the academic year of 1894–95 Meyer had been elected to be the Rector of the University of Tübingen, the exercise of the duties of which position had scarcely been relinquished when, on the evening of the 11th of April of last year, whilst busily engaged in his garden —a form of recreation in which Meyer from the days of his residence

at Rastede had continued to delight—he felt the symptoms of an approaching illness. Shortly after entering the house he became unconscious, and at 11 o'clock, six hours from the time of the first attack, Lothar Meyer passed quietly away, surrounded by those endeared to him by the highest of all worldly relationships.

And whilst in the sudden death of Lothar Meyer we mourn the close of the life of a man in the full enjoyment of bodily vigour and of a ripened intellectual activity, whose lovable simplicity of character, whose honesty of purpose, whose breadth of sympathy had endeared him to a wide circle of life-long friends and colleagues, our sorrow is as great at the loss to science of one whose unremitting labours in so many of its branches have enriched it with incalculable gain.

Lothar Meyer's scientific publications embrace a remarkable variety of subjects and display intellectual attainments which find him alike at home, whether in the devising of experiments for lecture illustration, the designing of apparatus to supply some want experienced in the laboratory, or needed for the conduct of the investigations of physical constants, or in the extension of chemistry by literary labours and theoretical speculations.

As I have already mentioned, Meyer's first experimental investigations belong to the domain of Physiological Chemistry, and of these the two most important are those concerned with the investigation of the chemistry of the blood. The first paper "On the Gases of the Blood," was published in 1856, in the *Zeitschrift für Rationelle Medicin*, and was undertaken with the object of elucidating the question of the conditions under which the gases exist in the blood. To solve, in fact, the question, then an open one, as to whether or no the gases are simply absorbed by the blood in quantities subservient to Dalton and Henry's law, that is, in amounts determined by alterations in pressure. The paper, an abstract of which, from the pen of Sir Henry Roscoe, appeared in the *Philosophical Magazine* of 1857, contains a detailed description of the method and apparatus used, and the results of the analyses of the gases expelled by boiling measured volumes of blood diluted with water free from air in a vacuous apparatus. The proportion of carbon dioxide existing in a state of combination was also determined by acidifying with a few crystals of tartaric acid the blood from which the gases had been previously expelled.

The absorption by defibrinated blood of oxygen, carbon dioxide, and nitrogen was also submitted to a carefully conducted quantitative investigation, and with the object of throwing further light upon this all-important subject, the behaviour of solutions of sodium car-

bonate towards carbon dioxide, and to this gas when mixed with others, for example, hydrogen, was examined.

Meyer, by this investigation, placed the chemistry of the gases of the blood upon a firm experimental basis, proving that the views held at that time were not in accordance, but rather in direct opposition to the facts brought to light by his experiments. Whereas, according to the older doctrines, the gases oxygen and nitrogen were simply absorbed by the blood, and chemical affinity was called in to explain the manner in which the blood takes up and gives off carbon dioxide, the reverse would appear to more nearly represent the facts. The greater portion of the oxygen taken up by the blood was proved by Meyer to be in amount independent of the pressure, and to exist in the blood in a state of loose combination with some one of its constituents.

The assumption that in the tissues the carbonate of soda in the blood is converted into the bicarbonate, and that this compound gives up some of its carbon dioxide in the lungs, and thus again forms the carbonate, is shown to be essentially improbable. Such a series of chemical changes being entirely unnecessary, as the absorption of the carbon dioxide and the liberation of this gas from the blood, find an all sufficient explanation in the laws regulating the absorption of gases by liquids.

Marchand's observation that no carbon dioxide is produced when oxygen is passed through defibrinated blood which has been previously freed from its absorbed carbon dioxide, is confirmed by one of Meyer's experiments, thus demonstrating the highly improbable nature of the hypothesis that carbon dioxide is produced by the immediate oxidising action of the oxygen in the blood. That the oxygen existing in the blood loosely combined with one of the blood constituents can easily pass into other and more stable modes of combination is demonstrated by an experiment made in the course of this investigation.

It has already been mentioned that in determining the amount of the gases contained in the blood, the latter, after dilution with water free from air, was boiled and the gases so expelled, collected, measured, and analysed. The proportion of combined carbon dioxide was ascertained by adding crystals of tartaric acid to the diluted blood which had been previously boiled, and the gas liberated by the acid was collected and its volume measured. Meyer observed that if the acid be added before the gases are removed, the bulk of the oxygen is not driven off by boiling, a fact abundantly proved by experiments specially made to test the truth of this observation, and shown in the following tabulated results of the analyses of the gases obtained from two samples of blood taken in quick succession,

(1) after treatment of the diluted blood at once with tartaric acid, (2) after the ordinary method of extraction.

Volume of Gases, at 0° and 760 mm. pressure, obtained from 100 Volumes of Blood.

	I.	II.
Oxygen	3·79	18·42
Nitrogen	2·94	4·55
Free carbon dioxide.....	—	5·28
Combined carbon dioxide...	—	20·97
Total carbon dioxide	27·10	26·25

This observation, demonstrating as it does that the loosely held oxygen readily enters into more stable combination with some constituent of the blood, shows clearly also that this oxidising action is not likely to occur in the blood vessels themselves, by reason of the alkalinity of the blood itself; but in the tissues, some of which are known to contain free acid, conditions favourable to such changes may frequently occur.

The conclusions drawn by Meyer from this investigation form the teaching accepted at the present day, and are summarised at the close of the paper in the following words :—

"*Das Blut trägt in seiner eigenen Zusammensetzung den Regulator für die Aufnahme dieses wesentlichsten Lebensmittels. Unabhängig vom wechselnden Drucke der Atmosphäre, zieht das Blut in den Lungen den Sauerstoff in richtigen Verhältnisse an, um ihn den Organen zu zubringen. Nur eine Veränderung des Blutes selbst bedingt eine erhebliche Veränderung der aufgenommenen Quantität: jede Blutentziehung wird daher zu einer Sauerstoffentziehung.*"

This first publication of Lothar Meyer's, whether it be regarded from the stand-point of the skill displayed in devising means to solve the problem in question and in carrying out the experimental work with care and exactitude, or from the attractive manner in which the results of the investigation are described and the careful consideration of the conclusions which the results appear to warrant, is justly entitled to a position amongst the classics of science.

Our knowledge concerning the "gases of the blood" received a further extension by the results obtained in the examination of the action of carbon monoxide on the blood. The results of this enquiry show that this gas is taken up by the blood under conditions similar to these regulating the behaviour of the latter towards oxygen: entering like oxygen into a loose state of combination with some constituent of the blood, and capable of expelling and replacing volume for volume the oxygen existing in combination with this substance.

Facts which offer a simple explanation of the poisonous action of carbon monoxide. Preliminary experiments made to discover the nature of the constituent of the blood which exercises this attraction for oxygen and carbon monoxide were, owing to the interruption of the investigation, never brought to a successful issue. Some seven years after the publication of this paper, Hoppe-Seyler succeeded in isolating this constituent of the blood, which he named Hæmoglobin (*Virchow's Arvhiv*, 1864, **29**, 233).

Whilst at Breslau, Meyer published an account of a complete examination of the waters from the springs at Landeck, in Prussian Silesia, papers having more than local interest. They contain a description of a method for estimating the carbon dioxide in natural waters dependent on the removal of the gases by means of a mercurial air-pump, instead of expelling them by boiling, and further attention is directed to the large proportion of nitrogen gas held in solution by the waters from these springs. This last mentioned fact is more than ordinarily suggestive at the present time in the light of the brilliant discoveries of Lord Rayleigh and Professor Ramsay.

It was during this period also that in conjunction with Heidenhain an investigation was undertaken on the absorption of carbon dioxide by aqueous solutions of neutral sodium phosphate in order to determine the question at issue between Pagenstecher's statement (1840), afterwards confirmed independently by Marchand (1843), and Liebig (1847), and the experimental results of Fernet (1858). Meyer and Heidenhain were successful in refuting the conclusions of the last named investigator and placed the subject in a clear light, explaining the production of the sodium bicarbonate in this instance as a mass action in terms of the teachings of Berthollet.

These investigations belong to the early period of Meyer's experimental work, which, until he became Professor at Carlsruhe, and finally passed to the still more congenial surroundings and duties of a University Professorship at Tübingen, were conducted under not altogether favourable circumstances.

Whilst at Carlsruhe and Tübingen, Meyer's powers as an investigator are shown in a long series of publications, dealing with questions pertaining to inorganic, organic, and general chemistry.

Instead, however, of attempting to discuss the individual communications, it will undoubtedly be more worthy of and befitting the occasion upon which we are met if I direct attention to those investigations and speculations which have exercised no unimportant influence in chemistry during the past 30 years.

Amongst these we have in the first place to consider the part Lothar Meyer took in the development of the great generalisation known

under the name of the "Periodic Law," or the "Natural System of the Chemical Elements." One of his last literary tasks was the editing for publication in the series of Classical Papers, published under the direction of Professor Ostwald, the papers of Döbereiner and von Pettenkofer dealing with the relationships exhibited by the atomic weights of the elements and their physical and chemical properties. In an appendix to these papers, and in the explanatory notes is given an account of the extension which the conception of Döbereiner and von Pettenkofer received at the hands of Dumas, Gladstone, Cooke, Odling, and others. This subject, some 11 years ago, provided the material for a lecture delivered by Meyer at Plochingen (on January 25th, 1885), entitled "*Ueber die neuere Entwickelung der Atomlehre.*" After reviewing the earlier attempts to discover relationships between the numerical values employed to represent the atomic weights of the elements, Meyer continues:—

"When at the commencement of 1860 I undertook the preparation of a work which should place before chemists and other men of science the most important of the laws relating to the atoms and their compounds, I soon discovered that by the adoption of the new atomic weights a much greater uniformity existed in the relationships between the numbers representing the atomic weights, than had hitherto been observed. At the same time there was shown a regular and continuous change in the valency of the elements from family to family, when the families are arranged in the order of the atomic weights of their members. I drew up at that time the following Table I, and also directed attention to the fact that the first differences, with the exception in the case of beryllium the atomic weight of which was still uncertain, were approximately 16, the two following differences approximated to 46, and the last were very nearly double this, namely 87—90."

"These last two sets of differences are repeated in the groups in the following table II, in which the first members are wanting.

"These groups were also arranged in the order of the atomic weights, with the exception of the last, which, because it consisted of 'members of uneven saturating capacities' ('*Sättigungs-capacität*'), appeared to me somewhat doubtful. At the same time, I did not overlook the fact that these groups could be arranged to make one complete table by placing them to the left of those in Table I, and thus placing cadmium before tin, and mercury before lead. The attempt to arrange all the elements in a single table was not successful, inasmuch as certain erroneous atomic weights, namely, Mo = 92, V = 137, and Ta = 137·6, exhibited differences which led me to formulate the two groups contained in Table III, which groups

TABLE I.

	Tetravalent.	Trivalent.	Divalent.	Monovalent.	Monovalent.	Divalent.
	—	—	—	—	Li = 7·03	(Be = 9·3?)
Difference	—	—	—	—	16·02	(14·7)
	C = 12·0	N = 14·04	O = 16·00	F = 19·0	Na = 23·05	Mg = 24·0
Difference	16·5	16·96	16·07	16·46	16·08	16·0
	Si = 28·5	P = 31·0	S = 32·07	Cl = 35·46	K = 39·13	Ca = 40·0
Difference	$\frac{89·1}{2}$ = 44·55	44·0	46·7	44·51	46·3	47·6
	—	As = 75·0	Se = 78·8	Br = 79·97	Rb = 85·4	Sr = 87·6
Difference	$\frac{89·1}{2}$ = 44·55	45·6	49·5	46·8	47·6	49·5
	Sn = 117·6	Sb = 120·6	Te = 128·3	I = 126·8	Cs = 133·0	Ba = 137·1
Difference	89·4 = 2×44·7	84·4 = 2×43·7	—	—	71 = 2 × 35·5	—
	Pb = 207·0	Bi = 208·0	—	—	(Tl = 204?)	—

TABLE II.

	Tetravalent.	Tetravalent.	Tetravalent.	Divalent.	
	Mn = 55·1 Fe = 56·0	Ni = 58·7	Co = 58·7	Zn = 65·0	Cu = 63·5
Difference	49·2 43·3	45·6	47·3	46·9	44·4
	Ru = 104·3	Rh = 104·3	Pd = 106·0	Cd = 111·9	Ag = 107·94
Difference	92·8 = 2×46·4	92·8 = 2 × 46·4	93·0 = 2 × 46·5	88·3 = 2 × 44·2	88·8 = 2 × 44·4
	Pt = 197·1	Ir = 197·1	Os = 199·0	Hg = 200·2	Au = 196·7

could not in any way consistently be brought into arrangement with the other elementary bodies."

TABLE III.

	Tetravalent.	Hexavalent.
	Ti = 48·0	Mo = 92
Difference	42·0	42
	Zr = 90·0	Vd = 137
Difference	47·6	47
	Ta = 137·6	W = 184

Such then in brief is Lothar Meyer's own account of the inception of the classification of the elements, which finds a place in the first edition of the *Modernen Theorien*. The development of this subject in Meyer's mind is shown in the sketch of a system of the elements, which, in manuscript form, Lothar Meyer handed, in July, 1868, to his successor in Eberswalde, Dr. Adolf Remelé ("Ostwald's Classiker der exakten Wissenschaften, No. 68, Karl Seubert. Zur Geschichte des Periodischen Systems," *Zeit. anorg. Chem.*, 9, 334).

This table, which is reproduced below (*vide* Table IV), bears undoubted evidence of having been prepared for a possible new edition of the *Modernen Theorien*. The mark § 91, which corresponds to the section in the first edition of the *Modern Theories* dealing with this subject, and the series of references given at the foot of the table both justify this conclusion.

The table contains two elements, namely, chromium and aluminium, in addition to those contained in the three tables of groups, and in some particulars certain elements have been rearranged; thus iron displaces nickel, the latter being placed by itself between cobalt and copper, whilst chromium occupies a similarly isolated position and that of aluminium remains doubtful. Meyer himself appears to have entirely overlooked the existence of this sketch until it was shown to him by Dr. A. Remelé in 1893, on the occasion of his lecture, delivered to the Chemical Society at Berlin.

The redetermination of the atomic weights of niobium and tantalum by Marignac in 1865, and of vanadium by Roscoe in 1867, opened the way for further progress.

In a comparatively short paper, dated from Carlsruhe, December, 1869, and contributed to *Liebig's Annalen* (*Annalen*, VII, Supplementband 1870, 5, 354—364), Lothar Meyer showed his appreciation of the advantages the new atomic weights offered, and how with these new values some 56 elements including all those elements, save

TABLE V.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
	B = 11·0	Al = 27·3		—		?In = 113·4		Tl = 202·7
	C = 11·97	Si = 28·0	—	—	—	Sn = 117·8	—	Pb = 206·4
	N = 14·01	P = 30·9	Ti = 48·0	As = 74·9	Zr = 89·7	Sb = 122·1	—	Bi = 207·5
	O = 15·96	S = 31·98	V = 51·2	Se = 78·0	Nb = 93·7	Te = 128?	Ta = 182·2	—
—	F = 19·1	Cl = 35·38	Cr = 52·4	Br = 79·75	Mo = 95·6	I = 126·5	W = 183·5	—
			Mn = 54·8		Ru = 103·5		Os = 198·6?	
			Fe = 55·9		Rd = 104·1		Ir = 196·7	
Li = 7·01	Na = 22·99	K = 34·04	Co = Ni = 58·6	Rb = 85·2	Pd = 106·2	Cs = 132·7	Pt = 196·7	—
?Be = 9·3	Mg = 23·9	Ca = 39·9	Cu = 63·3	Sr = 87·0	Ag = 107·66	Ba = 136·8	Au = 196·2	—
			Zn = 64·9		Cd = 111·6		Hg = 199·8	

hydrogen—the atomic weights of which had been determined either by the aid of Avogadro's law or the law of Dulong and Petit—could, together with the two elements beryllium and indium, be arranged in one table.

In this table, reproduced in Table V, it will be noticed that, as in its predecessor, the members forming the families are arranged in a horizontal series; there are many gaps which, as Meyer points out, may be at some time occupied by those elements whose atomic weights had not yet been accurately determined, and possibly by others yet to be discovered. Further, attention is drawn to the fact that the elements in the vertical columns IV, VI, and VIII exhibit many relationships, *e.g.*, isomorphism in certain of their compounds to the elements in the horizontal series immediately above. For example, titanium is so related to silicon and tin, vanadium with phosphorus and arsenic, chromium with sulphur and selenium, manganese with chlorine, copper and silver with gold, zinc with magnesium and calcium. It is evident from this statement, and also from the table, that Meyer fully appreciated the relationships in the properties of these elements upon which is based the division of the groups of elements into a main and a sub-group as in the system adopted at the present time, namely, the more completely extended one of Mendeléeff. Of Mendeléeff's work in the same direction, Lothar Meyer was as fully cognisant as the abstract of the communication of the former, "*Ueber die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente*," which appeared in the *Zeitschrift für Chemie* for 1869, could make him. In fact, Meyer describes his own table as in essence identical with that published by Mendeléeff, and further prefaces the statement respecting the series of relationships just referred to with the words: "I will *only* add one remark to those made by Mendeléeff in explanation of his table."

But, as it is not my intention to discuss any question of priority, but simply to lay before you an account of the part Lothar Meyer took in the development of this generalisation which has so profoundly influenced chemical thought, let us, therefore, return to other matters suggested by this paper "On the Nature of the Chemical Elements as a Function of their Atomic Weights." The perusal of this work indicates that its author is inclined to regard as evidence of the probable composite nature of the elementary atoms, the existence of these relationships between the properties of the elements and their atomic weights, the interdependence between which he summarises by describing the properties of the elements as periodic functions of the atomic weights.

To obtain a complete understanding of the nature of the elements

in their dependence on the magnitude of their atomic weights, it is necessary to follow step by step the changes of each property as we pass from element to element. The paper now under consideration, memorable as it is in so many ways, is especially so, in the example it affords of the first attempt to make such a detailed study of these changes. Lothar Meyer selected for this purpose the atomic volumes of the elements, the relation between which and the atomic weights is depicted in a graphic representation, which shows the atomic volume to be a periodic function of the atomic weights, with regularly distributed maxima and minima. The curve which represents these changes is divided by five maxima into six sections, which exhibit the form of a series of chains placed in a line. There is a strong resemblance between the second and third sections, and between the fourth and fifth sections. In the second and third sections, the atomic weight increases by 16 units in each, whilst in the fourth and fifth the increase is approximately 46. The curve not only exhibits, as Meyer pointed out, the variation in the atomic volumes of the elements, but also indicates that the fusibility, volatility, malleability, brittleness, electro-chemical behaviour, and other physical and chemical properties alter in like manner, consequently the properties of an element are determined by its position on this curve. For example, the easily fusible, volatile, and gaseous elements are to be found on the ascending branches of the curve, whereas the infusible elements are found either at the minima or on the descending sections. The elements, therefore, whose molecules are easily separated from one another, would experience an increase in their atomic volume in passing by addition to their atomic weight into the next element. Whereas the infusible and non-volatile elements, were it possible to convert them into the neighbouring element by increasing their atomic weights, would suffer a diminution in their atomic volume.

But the utility of this systematic study of the alteration in the atomic volume of the elements is not to be found alone in the beautiful epitome of the periodic law shown by this curve, but also in the revelation of errors in the determination of the atomic weights of many elements, and of the indication of the probable position in the "natural system" of elements such as indium and thallium, so entirely justified by the results of subsequent investigation.

In the conclusions set forth in this memoir are to be found the natural and independent consequences of the train of thought suggested by the classification of the elements given in the first edition of the *Modernen Theorien*, they form a statement and amplification of the law underlying the relation between the properties of the elements and the atomic weights, showing how fully Lothar Meyer had grasped

its meaning, and the justice of the action of the Fellows of the Royal Society of this country in awarding in 1882 the Davy Medal simultaneously to Mendeléeff and Meyer, as founders of this great and important generalisation, the "Periodic Law." No one has shown his high appreciation of the labours of Mendeléeff in this domain of speculation more than Meyer himself, as a perusal of the *Modernen Theorien* will show; and in the lecture delivered at Plochingen, to which I have already referred, Meyer speaks of Mendeléeff's brilliant contribution as forming "the coping stone of the building which in the course of years has been erected on the foundation of Döbereiner's Triads, of a work which did not, like Pallas Athene, spring ready armed from the head of a Jove, but has been gradually completed by the slow, painstaking, and often apparently vain endeavours of a whole series of workers."

The verification and justification of Mendeléeff's boldly conceived use of this law have undoubtedly contributed to effect a complete change in the attitude of chemists toward speculations of this kind, and have served to awaken an interest in the labours of our fellow countryman, Newlands, the value of whose contributions we should all the more willingly recognise when we recall the unsympathetic reception they received at the time, and the inappreciative remarks they called forth.

The little reward obtained by the efforts of those who, prior to 1860, had devoted much time and ingenuity to the study of these relations, finds a ready explanation in the confusion which existed in the minds of chemists as to the meaning of the term "atom," and the lack of agreement as to the definite representation of atoms.

Many of the Fellows of this Society there are who are able vividly to recall those times, and the tumult engendered by the contending systems; others, again, less fortunate, perhaps, than they, entirely dependent upon the knowledge acquired from the records of the science, can only by the aid of the imagination attempt to appreciate aright the condition of chemical thought at that time. To many it will be difficult to conceive that almost half a century after Dalton's atomic theory had been given to the world it should have been necessary for a speaker, at the memorable Conference of Chemists, held at Carlsruhe in September, 1860, to emphasise the inadmissibility of using more than one atomic weight for a given element, and to state that one value alone can be accepted as the true atomic weight of an element. Yet such indeed was the case, for, as Meyer himself tells us in the notes appended to Cannizzaro's famous pamphlet, "*Di un Corso di Filosofia Chemica*" (which in 1891 he edited for Ostwald's *Chemical Classics*), that one of the speeches which greatly contributed

to the advance of the atomic theory was that delivered by Professor Odling, of which this thought was the burden.

And when once we have realised something of the spirit of those days and the doubts and uncertainties which must have reigned in the minds of many chemists concerned with the definition of the conception so important to the vitality and growth of our science, we shall the more readily appreciate the sense of peaceful security which the repeated reading of Cannizzaro's pamphlet produced in Lothar Meyer's mind. The discovery of the Periodic Law may assuredly be counted as one, perhaps not the least of the benefits which have followed from the explanation given by the great Italian chemist of the apparent contradiction between the law of Avogadro and that of Dulong and Petit.

Many of Meyer's and his pupils' investigations were undertaken with the object of furthering the systematisation of inorganic chemistry and placing this portion of the science in a position similar to that which obtains in organic chemistry. In a paper entitled "*Zur Systematik der anorganischen Chemie*," published in the *Berichte* of 1873, expression was given to the wish for a change in this direction, and his brother chemists were exhorted to undertake a careful and searching examination of the already known compounds of the different elementary bodies, and to set on foot systematic investigations of the compounds of the elements of the several groups, and thus provide material for a "comparative chemistry."

As a step in the direction of systematisation, Meyer, in this paper, shows how it is possible to deduce the composition of the oxides and hydroxides of the elements by a general formula

$$H_{2n}X_2O_{v+n},$$

in which x represents the element, v the valency deduced from the composition of its highest oxide, a number identical with that representing the group in the natural system to which the element belongs for which to prevent confusion, the term "index of affinity" is proposed, and n is a small whole number. Applying this to the members of the third series we obtain the following.

	V = 1.	V = 2.	V = 3.	V = 4.	V = 5.	V = 6.	V = 7.
$n = 0$	Na_2O	Mg_2O_2	Al_2O_3	Si_2O_4	P_2O_5	S_2O_6	Cl_2O_7
$n = 1$	$H_2Na_2O_2$	—	$H_2Al_2O_4$	$H_2Si_2O_5$	$H_2P_2O_6$	$H_2S_2O_7$	$H_2Cl_2O_8$
			&c.,	&c.			

In like manner, formulæ for compounds of lower stages of oxidation may be deduced by the use of formula $H_{2n}X_2O_{v+n-2}$, $H_{2n}X_2O_{v+n-4}$, and so on.

Amongst the immediate results of this appeal are to be counted the investigations of the chlorides and oxychlorides of molybdenum,

chromium, and sulphur undertaken by several of Meyer's pupils. To these may also be added the investigations of Michaelis, which resulted in the discovery of the tetrachloride of sulphur; the dissociation of the latter and the conditions under which it is resolved into sulphur dichloride and chlorine afford another example of the influence of temperature on the valency exerted by any given element.

In the irrational treatment of inorganic chemistry, as depicted in the majority of chemical handbooks, Meyer found a state of affairs similar to that existing in organic chemistry, which 20 years previously Laurent had so rigorously criticised in his *Méthode de Chimie*. To Meyer the same causes appeared to be operative in retarding the progress toward the goal, the attainment of which would be the founding of a system of inorganic chemistry which "would not fear comparison with the thoroughly developed system of organic chemistry." (*Modern Theories*, p. 170.)

Meyer's lecture before the German Chemical Society, delivered in 1893, *Ueber den Vortrag der anorganischen Chemie nach dem Natürlichen Systeme der Elemente*, should surely contribute to place the "prize" more within our reach, for in this discourse he has shown how, by the adoption of certain "artifices" the natural system of the elements may be made the basis of a course of instruction in general inorganic chemistry. Not the least of the advantages of the method of treatment described in this lecture are those which accrue from the insight afforded into the history of the foundation of modern chemistry, and the gradual manner in which facts are laid before the student forming materials which serve to exemplify the laws of chemical combination and the development from these of the molecular atomic theory. The student thus instructed, and having acquired an understanding of atomic weights is prepared for an explanation of the outlines of the natural system. This outline is gradually filled in, not by a description and illustration of the properties of the elements and their compounds, group by group, but first by the facts brought to light in the study of the chief types of hydrogen compounds, and the subsequent systematic treatment of the elements forming the several groups or families in the "natural system."

It must be conceded that a student so instructed should form a higher conception of inorganic chemistry than many appear to do, and may possibly be inspired with the desire to devote his energies to add something which may help to make the system more perfect, for so suggestive a treatment could not fail to bring out with due prominence those points on which additions to our knowledge are so much to be desired.

No account of Meyer's labours in the department of chemistry

now under consideration would be complete without a reference to the work published by him in conjunction with Professor Seubert in 1883, in which are given the results of a recalculation of the atomic weights of the elements. The task was begun by Lothar Meyer himself in Eberswalde in 1867, and, after many years' interruption, recommenced and completed, as stated above, with the help of Professor Seubert. To some perhaps the task Meyer imposed upon himself may appear an almost thankless one; not so, however, to Meyer, who saw in the study of the modes of combination of the atoms "a new epoch in the history of chemical statics," and in the study of chemical change the basis of the "dynamics of the atoms."

To one so minded the reward for the unremitting labour, the time and energy consecrated to the work, would be found in placing upon a certain and sure foundation these fundamental constants, so essential to the advancement of the mechanics of the atoms.

The influence of Meyer's training in mathematics and in mathematical physics is evinced both in his experimental work and in his writings, and is shown in the selection of the problems submitted to experimental inquiry, the successful solution of which is to be attributed to the happy conjunction of the mathematician with the experimentalist. This is especially true of the series of investigations on the molecular volumes of chemical compounds, which had its starting point in the results obtained by calculation of the molecular volumes of certain gases from Graham's observations on the rates of "transpiration." From Graham's results, Professor Oskar E. Meyer deduced the coefficients of friction for the 19 gases experimented on, and by the aid of the relation established by Maxwell between the rate of transpiration or the coefficient of friction, the molecular weight, the molecular velocity and molecular sectional areas, Lothar Meyer calculated the molecular volumes for these 19 gases. He discovered that the volumes so obtained exhibit a ratio similar to that exhibited by the molecular volumes deduced for these gases by the aid of Kopp's law, employing the atomic volumes calculated from liquid compounds; and he established the fact that the molecular volume of a gas is the sum of the atomic volumes of its constituents. To institute a comparison between the values obtained for the molecular volumes in accordance with Kopp's rules and those deduced from the coefficients of friction, the latter, which are purely relative values, were expressed in terms of the molecular volume of liquid sulphur dioxide. In 12 cases, the agreement between the two sets of values is satisfactory, as will be seen by an inspection of the following table in which are given the molecular volumes arrived at from the friction constants, and also those calculated from the molecular volumes of liquid compounds. The agreement is more complete

when, in the cases of nitrogen and hydrogen and the compounds containing these elements, the atomic volumes obtained from the friction constants are employed, as will be seen by a comparison of the values contained in the third column, in which the molecular volumes are calculated with these numbers. It is further worthy of remark that in the case of carbon monoxide and of carbon dioxide a greater concordance is observed between the molecular volumes based upon the friction constants, and the calculated values, when Kopp's lower value for oxygen is used, that is, for oxygen combined as it is in water, instead of the higher value for oxygen as it is assumed to be combined in the "carbonyl" group.

Molecular Volumes of Gases.

	From friction.	Calculated by aid of Kopp's numbers.	
	I.	II.	III.
Oxygen	13·8	15·6	15·6
Nitric acid	15·9	14·5	15·5
Carbon dioxide	26·7	31·0	26·6
Hydrogen chloride .	24·1	28·3	25·8
Chlorine	44·1	45·6	45·6
Sulphur dioxide....	43·9	42·6	42·6
Hydrogen sulphide.	30·0	33·6	28·6
Methylic chloride..	48·2	50·2	42 8
Ammonia	23·6	18·8	16·7
Cyanogen.....	55·1	56·0	56·0
Ethylic chloride....	66·0	72·3	59·8
Methylic ether	53·8	62·8	47·8
Air	15·0	—	15·0
Nitrogen	15·3	4·6	15·3
Carbon monoxide ..	15·4	23·2	18·8
Nitrous oxide.....	15·7	16·8	27·5
Methane.....	19·4	33·0	23·0
Ethylene.....	33·6	44·0	34·0
Hydrogen.....	6·0	11·0	6·0

Our interest in these results is due not alone to the fact that they contribute to the advancement of knowledge, but also that they are deductions from some of the valued experimental facts bequeathed to science by one of the founders of this Society and its illustrious first President, Thomas Graham.

Lothar Meyer sought next to extend these observations on gases by determining experimentally the rates of transpiration of vapours; the work was commenced in Carlsruhe, and continued in Tübingen,

the paper containing the results of the first stage of this inquiry being dated from the latter place. In the account given in the *Annalen der Physik und Chemie* (N.F., 1879, **7**, 497), the method of observation and the apparatus employed are described. The apparatus devised for this purpose is a beautiful example of the same inventive skill which characterises all Meyer's work, and compels our admiration. The rate of transpiration measured is that of the saturated vapour. A long series of experiments were made with benzene, showing (1) that in case of vapours the coefficient of friction increases with a rise in temperature more rapidly than in the case of gases, (2) that the molecular volume of vapours is greater at lower than at higher temperatures, which is also true of gases.

The careful and searching criticism to which Meyer submitted the experimental data revealed the fact that the laws governing the transpiration of gases cannot without modification be applied to vapours, and that further information as to the influence of pressure and of temperature on the vapour of benzene is required. Empirically he arrived at an expression for the relation between the rate of transpiration and the pressure of saturated vapours. From the constancy of this quantity is deduced a relationship between the coefficient of friction of benzene vapour, and possibly of all other saturated vapours; namely, that the coefficient of friction is proportional to the square root of the tension of the vapour.

In conjunction with O. Schumann and subsequently with V. Steudel, the rates of transpiration of a number of fatty acids and their ethereal salts, and also of several series of homologous compounds were determined. The results of these extended observations show that in the majority of cases, homologous compounds have very nearly the same coefficient of friction. The average values being for

Alcohols, $C_nH_{2n+2}O$	$\eta = 0{\cdot}000142$
Chlorides, $C_nH_{2n+1}Cl$	$\eta = 0{\cdot}000150$
Esters, $C_nH_{2n+1}O_2$	$\eta = 0{\cdot}000155$
Bromides, $C_nH_{2n+1}Br$	$\eta = 0{\cdot}000182$
Iodides, $C_nH_{2n+1}I$	$\eta = 0{\cdot}000210$

The influence of the nature of the atoms constituting the molecules is shown by a comparison of chlorides, bromides, and iodides of approximately the same molecular weight. The influence exerted by the iodine is found to be greater than that of the bromine, and this again than that of chlorine.

The molecular volumes of these various compounds calculated from the friction constants exhibit a proportionality to those values obtained from their molecular volumes in the liquid state. When the

first of these values is expressed in terms of the molecular volume of sulphur dioxide, as was done in the case of the gases, the molecular volumes are then approximately half the molecular volumes for the same compounds in the liquid condition. That these two sets of values should not be identical finds a ready explanation in the fact that the molecular volume of a liquid increases with rise of temperature, whereas that of a vapour decreases.

Meyer further pointed out that in the case of the isomeric butyl compounds the sectional area of the molecule of the tertiary isomeride is less than that of the corresponding secondary, and this again than that of the primary compound; but he found no such regularity in the case of the isomeric propyl compounds.

A notable feature in the several publications on this subject is the unbiassed freedom with which the experimental results are discussed, and the care which is taken to avoid too hasty "generalisation." The difficulties of the solution of the problem of the influence of the several factors affecting the coefficient of friction of gases and its relation to the form of the molecules are fully realised and appreciated by Meyer, who is careful to direct attention to many matters which need a searching experimental examination before the full and true meaning of these phenomena is realised.

The numerous publications of the pupils of Lothar Meyer, emanating chiefly from the laboratories of Tübingen, are of a very diversified character. In the selection of subjects for investigation, and in the manner of execution, the influence of the master's spirit is to be traced. The preparation of compounds, both in inorganic and organic chemistry, has added to the list of compounds already known; the investigation of their modes of formation and properties has been so directed as to shed a light on points of general interest.

The physical constants of many series of compounds have been revised, and our knowledge of the relation between the physical properties and the composition and constitution of compounds received extension.

That interesting class of chemical changes usually described as "contact actions" has been submitted to careful and critical examination, and our knowledge of "oxygen carriers" and of "chlorine carriers" and their mode of action very materially advanced.

Measurements of the influences of mass, time, dilution, and of other factors in a variety of instances of chemical change, have added many new examples of the truth of the law of Guldberg and Waage.

This mere recital of the themes affords evidence of the undoubted attraction which the more theoretical side of chemistry had for Meyer, and at the same time show how strong was the desire

which animated him to aid in the ordering of the facts of chemistry and thus to contribute to the building up of a system of chemical philosophy.

We are also indebted to Meyer for many laboratory appliances, some of which are incidentally mentioned in the description of the results of some investigation, others again have formed the subject of special memoirs. The paper on "Air Baths" affords ample evidence of his ingenuity in devising apparatus, and also shows that by strict attention to scientific principles great efficiency can be combined with economy in fuel. In addition, the exact analysis of gases has been simplified by the apparatus devised by Lothar Meyer and K. Seubert, an account of which formed the subject of a paper contributed to the Transactions of this Society. At the same time Meyer drew attention to the advantages in the calculations of the results of gas analysis, which is secured by a strict adherence to Avogadro's law.

In the history of the progress of theoretical chemistry during the past 30 years, the name of Lothar Meyer must occupy a foremost position. To the advancement of chemical theory he not only contributed as a founder of the natural system of the elements, but also as an exponent of the speculations and theories, whether in chemistry or physics, which have combined to awaken an interest in those problems of physical chemistry, the solution of which will bring nearer the realisation of Berthollet's ideal, a chemical philosophy based on the general laws and principles of mechanics.

The first edition of *Die Modernen Theorien* was written not alone for chemists, but also to make known to other scientific investigators the nature of the hypotheses and theories forming the basis of chemical philosophy at the time. The time of publication of this work, namely, 1864, was indeed opportune, following as it did immediately on the acceptance by the majority of chemists of the new atomic weights. It marks an epoch in the growth of the atomic theory; the terms "atom" and "molecule" had at length acquired a distinct and definite meaning.

The publication of a book dealing solely with the theories of chemistry was a matter of great moment in its history, not to be undertaken in a light spirit, nor did Meyer approach the enterprise in any such mood, for only after it had practically been rewritten for a third time was the manuscript handed to the printer. Despite the labour and time expended on this work, the final step was taken with serious doubts as to the value and utility of it, and whether even its usefulness would prove a sufficient excuse for the violation of the accepted traditions of his co-workers in chemistry. These traditions allowed the indulgence in theoretical speculations, when these

appeared—one might almost say—as addenda to the results of experimental inquiry. This attitude of chemists to theoretical speculation suggests that in some occult way they had inherited that contempt for theory which Mephistopheles sought to implant in the mind of the pupil of the alchemist Faust.

"*Grau, theurer Freund, ist alle Theorie.*"

This disregard for hypothesis and theory is as little to be justified as is the other extreme. Chemical literature contains many examples of both faults, and certainly many of the text-books of the science would be better for the infusion of the quickening influence of chemical philosophy into the dry bones which masquerade as a portrayal of the science of chemistry.

Lothar Meyer's book has undoubtedly contributed to effect a change in this direction, and has also led to a more just appreciation and recognition of the truths contained in the hypotheses of Avogadro and of Dulong and Petit. At the time when this book appeared, Avogadro's law was by some regarded as purely arbitrary, the adoption or rejection of this hypothesis was considered of little import; it received allegiance from others on purely chemical considerations. To such the exposition given by Meyer of the application of these hypotheses in the determination of the atomic weights of the elements, the agreement in the deductions arrived at by their assistance, and the necessity of Avogadro's hypothesis recognised by Clausius on purely physical grounds, to which Meyer directed attention, must have proved convincing and have served to elevate these laws to a position of regard higher than that they had previously enjoyed.

The feature of the teaching of this work, summarised as we find it in the extended title *Die Modernen Theorien der Chemie und ihre Bedeutung für die chemischen Statik* is that which gives the distinctive character to the book. The determination of the atomic weights and the methods used become important, inasmuch as they are concerned with the measurement of the relative masses of the atoms, the invariable quantities, the constants of a theory of the statics of the atoms. The additional property of the elementary atoms, revealed by the consistent use of Avogadro's law, the specific quality which determines the atom-fixing power of an elementary atom, is studied in the light of an extension of this theory; and the formulæ employed to show the constitution of molecules become representations of the equilibrium of the atoms. The discovery of this property marks a new epoch in the history of chemical statics.

To the interpretation of the constitution of solid compounds whose molecular weights cannot be directly ascertained by Avogadro's law, this atom-combining power is extended, but not without

due caution as to the uncertainty surrounding the conclusions drawn. The physical properties of compounds are discussed and interpreted in the light of the new doctrine of valency, and finally this doctrine is applied to the classification of the elements in the manner I have already described.

With the appearance of the second edition, which was published in 1872, the book altered somewhat in character, the 147 pages of the first edition having grown into 364; this addition, in part due to the incorporation of empirical data illustrative of the theories, in part also, to the somewhat lengthy discussion and illustration of the laws of atomic linking, which the development of organic chemistry and of the benzene derivatives necessitated; and, finally, to the inclusion of an account of the notable additions made to our knowledge of the "nature of the chemical atoms," which the speculations of Meyer and of Mendeléeff had revealed.

To Meyer himself the second edition had assumed greater importance than its predecessor, and he ventured to dedicate it to his honoured master, Bunsen.

The third edition, published five years after the second, is not very materially different from the latter, although it contains an important contribution to the study of the nature of valency, in the recognition of the fact that the valency of an element may be influenced by the nature of the atoms with which it combines. Thus chlorine, bromine and iodine act as monovalent elements in their compounds with the more electropositive elements, such as hydrogen and the metals; whereas to oxygen and other electro-negative elements they comport themselves as polyvalent, and, possibly, heptavalent elements.

In the fourth edition, which was published six years after the third, and followed by a fifth a year afterwards, the *Modernen Theorien* underwent a very material alteration. To the discussion of the problems of chemical statics, which had been treated in former editions, a special part was added concerned with the phenomena of chemical change, and the influence of external agents in promoting or retarding chemical action. This third section deals with the "Dynamics of the Atoms," thus giving completion to the thought suggested by the earlier editions of the publication of a work which should form an account of "Chemical Mechanics."

The translation of the fifth edition of this work by Professor Williams and myself, which appeared in 1887, found so ready a sale that in three years the edition was exhausted, a fact which surely justifies the belief that the book is so well known amongst chemists as to preclude the necessity of an attempt to sketch in outline the contents of the third section of the work. The 20 years that have elapsed since the first appearance of Meyer's *Modernen*

Theorien have witnessed great changes in the attitude of chemists towards hypotheses and theories; a change which in some quarters has led to the institution of a comparison between the modern school of chemists and those of the classical school, not altogether favourable to the former. Be that as it may, there can be no doubt as to the advantages chemistry has already derived from the acceptance of the kinetic theories of the states of aggregation, of the kinetic theory of electrolysis of Clausius, and of Guldberg and Waage's theory of the action of mass; the necessity for some such hypotheses was pointed out by Meyer in the first edition of this book in the following passages.

"It will be necessary in the immediate future to introduce some new hypotheses. It appears that many of the fields of molecular physics which are closely allied to, and are in the almost exclusive possession of chemistry, cannot be successfully cultivated at present without the theoretical speculations and hypotheses advocated by Clausius, which represent the different conditions and forms of matter as determined by the various forms of motion of the corporeal molecules.

"These views, based on the fundamental principles of mechanics —and especially the mechanical theory of heat—alone appear capable of penetrating into the influence which the chemical nature of bodies —the atomic constitution of their molecules—exerts on the changes of the states of aggregation, *e.g.*, fusion and solidification, evaporation and condensation; on vapour pressure, and on the phenomena of diffusion, absorption, solution, crystallisation, endosmosis, and all similar processes. The theoretical investigation of electrolysis and of the whole field of electro-chemistry can only be successful from this side. In the consideration of all purely chemical reactions, chemical decompositions and chemical combination, such conceptions may become indispensable, in fact very similar ideas have been suggested by the consideration of purely chemical phenomena."

The fulfilment of this prediction has not yet been followed by the complete alteration in the old conception of "affinity" as an attractive force, a change also foreshadowed in the early editions of the *Modernen Theorien*. The causes which have been operative in retarding this advance in our conception of affinity are found in the absence of kinetic speculations on the thermal changes accompanying chemical phenomena. The discussion of the vast accumulation of thermochemical data from such a standpoint, as suggested by Meyer, not only in the last edition of the *Modernen Theorien*, but also in the article published in 1883 in the *Annalen* on the "Basis of Thermochemistry," and, again later, in the contribution to the *Zeit. physikal. Chem.*, entitled the "Evolution of the doctrine of Affinity,"

must bring nearer the realisation of a kinetic theory of chemical affinity.

Amongst the last undertakings of Meyer's active life was the preparation of a sixth edition of this work, which has played so important a part in directing attention to the theoretical side of the science of chemistry, and also in arousing an interest in the borderland between chemistry and physics, now cultivated with such zeal and enterprise, and with results so full of promise.

Lothar Meyer had repeatedly declined to undertake the task of preparing a new edition of the *Modern Theories*, and when I approached him, in 1890, he suggested that Professor Williams and I should prepare a translation of the smaller book which had just appeared. In Germany two editions of this book have been published, and it has also been translated into Russian.

When, two years ago, I again wrote to Lothar Meyer on the subject of a new edition of the *Modern Theories*, he replied that he had declined the invitation of his publishers, feeling that "it would be tempting fortune to undertake the republication of a work which had been so long before the public." He expressed himself as "perfectly content with the influence which it had exercised in the chemical world," but felt that a new edition must either be made much shorter or more extensive, and, foreseeing this, he had written the smaller one, namely, *The Outlines of Theoretical Chemistry*. He continues in his letter, "The world desires at the present time numbers and formulæ, and is no longer thoroughly alive to the philosophy set forth in the *Modern Theories*."

This decision was, however, overruled, and, on the day of his death, Meyer had completed the manuscript for Book I of the sixth edition, which has since been published, with a preface, by Professor O. E. Meyer, who has justly described it as "an interesting monograph on the atoms, of permanent value in itself."

Meyer's labours were not entirely confined to matters of a purely scientific character. Like many distinguished chemists in this country, he took a great interest in questions relating to education, and contributed many articles to magazines, &c., on this subject. We are so much accustomed to look to Germany as the ideal of systematised education, that we are scarcely prepared to see the faults which Lothar Meyer detected. The difference in standpoint sufficiently explains the direction of attack. The authorities of the German Universities have, from the first, recognised the equality of all branches of knowledge, and their right to a just recognition in all University education. Further, the rewards and degrees dispensed by them are not to be gained through the single avenue of examination and knowledge of the known, but evidence of

ability to utilise the known and to extend the bounds of knowledge is demanded from their graduates.

How beneficial this attitude has been to the development of the industrial enterprises of Germany is thoroughly understood by chemists. Hence Meyer was not concerned with the problems of technical education as we understand them in this country, but rather with the training of those who were to become students of chemistry in the Universities. For such he advocated a broad and liberal school training in mathematics and languages, and did not wish to see the time and training, which should be devoted to these fundamental subjects, curtailed by instruction in special branches of science carried to such a degree that, when the student comes to the University lecture-room, the subject has lost all its freshness and attractions for him; and he regards attendance at lectures as a waste of time, and nothing less than *eine Arbeit* will satisfy him in the laboratory. In England we may surely learn much from such suggestive thought; let the Universities demand, as Meyer advocated for Germany, evidence of a sound, liberal training before the student matriculates. Once matriculated, permit the undergraduate to pursue some well-defined course of special study, and ask as evidence of the result of such work, not the performance in an examination hall, but some contribution to chemical knowledge. The industries would then, as in Germany, look to the Universities for the thoroughly trained chemists to assist in their direction, and provide the scientific labour which must form a prominent feature in future chemical industrial enterprise.

Learned Societies in Germany, in this country, and in Russia have, like our own, sought to honour themselves by placing the name of Lothar Meyer on the roll of their distinguished members, and, with us, deplore the loss of one whose thought has left its impress on the annals of science, and who has shown by experimental work, distinguished alike by the conception, the execution, and the lucid description of results, how best the boundaries of knowledge may be extended.

The following list of the published works of Lothar Meyer and of his pupils is taken from Professor Seubert's account of the life of Meyer (*Ber.*, 1895, **28**).

I.

1.—Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik. Breslau. Maruschke and Berendt. Five editions; 1864, 1872, 1876, 1883, and 1884. (Translated into English and French.)

2.—Grundzüge der theoretischen Chemie. Leipzig. Breitkopf and Härtel, 1890. Second edition, 1893. (Translated into English and Russian.)

3.—L. M. und Karl Seubert. Die Atomgewichte der Elemente aus den Originalzahlen neu berechnet. Leipzig. Breitkopf and Härtel, 1883.

4*a*.—Abriss eines Lehrganges der theoretischen Chemie, vorgetragen von Prof. S. Cannizzaro. Herausgegeben von Lothar Meyer. *Ostwald's Klassiker der exacten Wissenschaften.* No. 30. Leipzig. Wilhelm Engelmann, 1891.

4*b*.—Die Anfänge des natürlichen Systemes der chemischen Elemente. Abhandlungen von J. W. Döbereiner und Max Pettenkofer, nebst einer geschichtlichen Uebersicht der Weiterentwickelung der Lehre von den Triaden der Elemente. Edited by Lothar Meyer. *Ostwald's Klassiker der exacten Wissenschaften.* No. 66. Leipzig. Wilhelm Englemann, 1895.

II. *Chemical Papers and Dissertations of his Pupils.*

1857. 5.—Ueber die Gase der Blutes. *Inaug. Diss.*, Würzburg, 1857; *Henle und Pfeuffer's Zeitschr. f. rat. Med.* [N.F.], **8**, 256. Abstract, *Pogg. Annalen*, **102**, 299; *Phil. Mag.*, 1857, **14**, 263—268.

1858. 6.—De sanguine oxydo carbonico infecto. Diss. Aug. Vratisl, 1858. Ueber die Einwirkung des Kohlenoxydgases auf Blut. *Henle und Pfeuffer's Zeitschr. f. rat. Med.* [N.F.], **9**, 83; *Schmidt's Jahrb. f. d. ges. Med.*, **101**, 22.

7.—Wirkung des Drucks auf die Verwandtschaft. *Pogg. Annalen*, **104**, 189; *Liebig's Annalen*, **110**, 312.

1862. 8.—L. M. und Rud. Heidenhain. Ueber die Absorption der Kohlensäure durch Lösungen des neutralen Natronphosphates. *Studien des physiol. Inst. zu Breslau.* Heft 2. Leipzig, 1863. Abstract, *Liebig's Annalen*, Suppl. II, 157.

1863. 9.—Krystallform des Desoxylsäureäthyläthers. *Pogg. Annalen*, **120**, 605.

10.—Bequeme Vorrichtung zur Reinigung des Quecksilbers. *Zeit. anal. Chem.*, **2**, 241.

11.—Gasometrische Bestimmung der Kohlensäure in Mineralwassern. *Zeits. anal. Chem.*, **2**, 237. *J. pr. Chem.*, 1864, 476—501.

1864. 12.—Ueber die Hofmann'sche Reaction auf Tyrosin. *Liebig's Annalen*, **132**, 156; *Zeits. anal. Chem.*, **3**, 199.

13.—Chemische Untersuchung der Thermen zu Landeck in der Grafschaft Glatz. *J. pr. Chem.*, 1864, 1.

1865. 14.—Ueber die Umkehrung der Natriumlinie. *Zeit. Chem.*, 1865, 464. *Phil. Mag.*, **30**, 390.

15.—Ueber die Beziehungen der Specifischen Wärme zum Atom- und Molekular-gewicht. *Zeit. Chem.*, 1865, 250.

1866. 16.—Ueber einige Zersetzungen des Chloräthyls. *Liebig's Annalen*, **159**, 282.

1867. 17.—Ueber die Molekularvolumina chemischer Verbindungen. *Liebig's Annalen*, Suppl. V, 129.

1870. 18.—Die Natur der chemischen Elemente als Function ihrer Atomgewichte. *Liebig's Annalen*, Suppl. VII, 354.

1871. 19.—Ueber die Apothese Avogadro's. *Ber.*, **4**, 25. Isomorphie von Natronsalpeter und Kalkspath. *Ber.*, **4**, 53.

1872. 20.—Apparat zur Regulirung des Luftdruckes der Destillationen. *Ber.*, **5**, 804. Ref.

1873. 21.—Beschreibung eines Druckregulators. *Liebig's Annalen*, **165**, 303.

1873. 22.—Ueber das Atomgewichte des Molybdins. *Liebig's Annalen*, **169**, 360.
23.—Zur Systematik der anorganischen Chemie. *Ber.*, **8**, 1627.
1875. 24.—Vorlesungsversuch über Verdampfung ohne Schmelzung. *Ber.*, **8**, 1627.
25.—Osc. Brenken. Ueber Chlorjod. *Ber.*, **8**, 487.
26.—Pet. Melikoff. Ueber die Dichte des aus Dreifachchlorjod entstehenden Dampfes. *Ber.*, **8**, 490.
1876. 27.—Wasserstoffentwickelung durch Zink und Kupfersulfat. *Ber.*, **9**, 512.
1877. 28.—Ueber Dreifachchlorjod. *Ber.*, **10**, 648.
29.—W. Bornemann. Ueber Chlorjod, Bromjod, Chlorbrom und deren Verhalten gegen Wasser. *Inaug. Diss.*, Tübingen, 1877. *Liebig's Annalen*, **189**, 183.
30.—Ueber unvollständige Verbrennung. *Ber.*, **10**, 2117.
31.—Emil Elsässer. Ueber eine Elektrolyse mit Wasserstoffentwickelung an beiden Polen. *Ber.*, **10**, 1.
32.—Otto Schumann. Ueber die Affinität des Schwefels und des Sauerstoffs zu den Metallen. *Inaug. Diss.*, Tübingen, 1877.
1878.—33.—John H. Long. Ueber die Einwirkung von Wasserdampf auf glühende Holzkohlen. *Liebig's Annalen*, **192**, 288.
34.—Ueber Transpiration von Dämpfen. *Ber.*, **11**, 206; *Wied. Annalen*, **1879**, **7**, 497.
35.—Ueber das Atomgewichte des Berylliums. *Ber.*, **11**, 576.
36.—Ludwig Schreiner. Ueber die Siedepunkte der Ester und Aether-Ester des Oxysäuren. *Inaug. Diss.*, Tübingen, 1878; *Liebig's Annalen*, **197**, 1.
37.—Georg Prätorius. Ueber die Salze der Chlorchromsäure. *Inaug. Diss.*, Tübingen, 1878; *Liebig's Annalen*, **201**, 1.
38.—Hans Settegast. Beiträge zur quantitativen Spectralanalyse. *Inaug. Diss.*, Tübingen, 1878; *Wied. Annalen*, [2], **7**, 242.
39.—Wilh. Püttbach. Ueber Molybdänacichloride. *Inaug. Diss.*, Tübingen, 1878; *Liebig's Annalen*, **201**, 123.
40.—Friedr. Clausnizer. Ueber einige Schwefeloxychloride. *Inaug. Diss.*, Tübingen, 1878. *Ber.*, **11**, 2007, 2009, 2011, 2012.
1879. 41.—Reinigung des Quecksilbers. *Ber.*, **12**, 437.
42.—Jul. Schuncke. Ueber die Löslichkeit des Aethyloxydes in Wasser und wässriger Salzsäure. *Inaug. Diss.*, Tübingen, 1879; *Zeit. physikal. Chem.*, **14**, 331.
43.—James Morris. Ueber den Einfluss der Masse auf chemischen Umsetzungen. *Inaug. Diss.*, Tübingen, 1879; *Liebig's Annalen*, **213**, 253.
44.—J. H. Long. On the diffusion of Liquids. *Inaug. Diss.*, Tübingen, 1879; *Wied. Annalen*, **9**, 613.
45.—Emil Elsässer. Ueber Galvanische Leitung von Metalllegirungen. *Wied. Annalen*, **8**, 455.
1880.—46.—Zur Geschichte der periodischen Atomistik. *Ber.*, **13**, 220, 259, 2043.
47.—Zu Victor Meyer's Dampfdichtebestimmung. *Ber.*, **13**, 991.
48.—Ueber das Atomgewichte des Berylliums. *Ber.*, **13**, 1780.
49.—Verdampfung ohne Schmelzung. *Ber.*, **13**, 1831.
50.—Paul Schoop. Die Aenderung der Dampfdichten bei variablem Druck und variabler Temperatur. *Inaug. Diss.*, Tübingen, 1880; *Wied. Annalen*, **12**, 550.

1881. 51.—Verdampfung ohne Schmelzung. *Ber.*, **14**, 718.
52.—L. M. und Otto Schumann. Ueber Transpiration von Dämpfen. *Ber.*, **14**, 593.
53.—Otto Schumann. Ueber Transpiration von Dämpfen. *Wied. Annalen*, **12**, 40.
54.—Emil Elsässer. Ueber die Specifischen Volumina des Esters der Fettreihe. *Inaug. Diss.*, Tübingen, 1881; *Liebig's Annalen*, **218**, 302.
55.—Konr. Bötsch. Unvollständige Verbrennung von Gasen. *Inaug. Diss.*, Tübingen, 1881; *Liebig's Annalen*, **211**, 207.
56.—Alb. Hölzer. Ueber einige Phenoläther. *Inaug. Diss.*, Tübingen, 1881.
57.—Eug. Sapper. Ueber die Einwirkung der Halogenwasserstoffe auf Zusammengesetzte Aether. *Inaug. Diss.*, Tübingen, 1881; *Liebig's Annalen*, **211**, 178.
58.—Theod. Lehrfeld. Ueber die Einwirkung von Ammoniak auf Bibrombernsteinsäure und auf Bibrombernsteinsäureäthylester. *Inaug. Diss.*, Tübingen, 1881. *Ber.*, **14**, 1816.

1882. 59.—Ueber die Bildung und Zersetzung des Acetanilids. *Ber.*, **15**, 1977.
60.—L. Gordon Paul. On the identity of certain mixed Ethers of Oxalic Acid. *Inaug. Diss.*, Tübingen, 1882.
61.—Victor Steudel. Ueber Transpiration von Dämpfen. *Inaug. Diss.*, Tübingen, 1882; *Wied. Annalen*, **16**, 369; see also Lothar Meyer, *Wied. Annalen*, **16**, 394.
62.—Ernst Noack. Ueber die Phenylester der Phosphorigen Säure. *Inaug. Diss.*, Tübingen, 1882; *Liebig's Annalen*, **218**, 85.
63.—Georg Kumpf. Ueber Nitrophenyl-Benzyl- und Nitrophenyl-Nitrobenzyläther und die Nitrirungsproducte des Benzylchlorids. *Inaug. Diss.*, Tübingen, 1882; *Liebig's Annalen*, **224**, 96.
64.—Rich. Brix. Ueber den Austausch von Chlor, Brom, und Jod zwischen organischen und anorganischen Verbindungen. *Inaug. Diss.*, Tübingen, 1882; *Liebig's Annalen*, **225**, 146.

1883. 65.—Ueber Luftbäder. *Ber.*, **16**, 1087.
66.—Die Grundlagen der Thermochemie. *Liebig's Annalen*, **218**, 1.
67.—Paul Spindler. Der Nitrirungsprocess der Benzolderivate. *Inaug. Diss.*, Tübingen, 1883; *Ber.*, **16**, 1252.
68.—Paul Frische. Ueber Nitrite *p*-Kresyl-Benzyl-Aether. *Inaug. Diss.*, Tübingen, 1883; *Liebig's Annalen*, **224**, 137.
69.—Martin Rapp. Ueber die Phenyl- und Kresylester der Phosphorsäure und ihre Nitrirung. *Inaug. Diss.*, Tübingen, 1883; *Liebig's Annalen*, **224**, 156.
70.—Benj. Köhnlein. Eine bequeme Darstellung der Paraffine. Communicated by Lothar Meyer. *Ber.*, **16**, 560.
71.—Benj. Kohlein. Ueber die Austausch von Chlor, Brom, und Jod zwischen anorganischen und organischen Halogenverbindungen. *Inaug. Diss.*, Tübingen, 1883; *Liebig's Annalen*, **225**, 171.

1884. 72.—Ueber einen empfindlichen Thermoregulator. *Ber.*, **17**, 478.
73.—Ueber Aetherester der Glycolsäure. *Ber.*, **17**, 669.
74.—Ueber die Berechnung der Gasanalysen. *Liebig's Annalen*, **226**, 115. On the calculation of Gas Analysis. *J. Chem. Soc.*, **45**, 601.
75.—L. M. und Karl Seubert. Ueber Gasanalysis bei starkvermindertem Druck. *Liebig's Annalen*, **226**, 87. Gas analysis under greatly reduced pressure. *J. Chem. Soc.*, **45**, 581.

1884. 76.—Alfr. G. Page. Ueber anorganische Chloride als Chlorüberträger. *Inaug. Diss.*, Tübingen, 1884; *Liebig's Annalen*, **225**, 196.

77.—Ad. Scheufelen. Ueber Eisenverbindungen als Bromüberträger. *Inaug. Diss.*, Tübingen, 1884; *Liebig's Annalen*, **225**, 196; **231**, 152.

78.—Aug. Fölsing. Ueber einige Aetherester der Glycolsäure und Salicylsäure. *Inaug. Diss.*, Freiburg, 1 B., 1884. Abstract communicated by Lothar Meyer. *Ber.*, **17**, 484 and 486. Compare also the note, *Ber.*, **17**, 669.

79.—Herm. Bauer. Ueber die Siedepunktsanomalien der chlorirten Acetonitrile und einige ihre Abkömmlinge. *Inaug. Diss.*, Tübingen, 1884; *Liebig's Annalen*, **229**, 163.

80.—G. Schlegel. Ueber die Verbrennung von Kohlenwasserstoffen, ihren Oxyden und Chloriden mit Chlor und Sauerstoff. *Liebig's Annalen*, **226**, 133.

1885. 81.—Ueber Chlor- und Brom-überträger. *Ber.*, **18**, 2017.

82.—Eisenchlorid als Jodüberträger. *Liebig's Annalen*, **231**, 195.

83.—L. M. und Karl Seubert. Ueber die Einheit der Atomgewichte. *Ber.*, **18**, 1089. On the unit adopted for Atomic Weights. *J. Chem. Soc.*, **47**, 426.

84.—L. M. und Karl Seubert. Das Atomgewicht des Silbers und Prout's Hypothese. *Ber.*, **18**, 1098. The Atomic Weight of Silver and Prout's Hypothesis. *J. Chem. Soc.*, **47**, 434.

85.—Joh. Lindner. Ueber Bromonitrophenole, Bromonitrophenetole, und deren Amidoderivate. *Inaug. Diss.*, Tübingen, 1885; *Ber.*, **18**, 611.

86.—Heinr. Spindler. Ueber den Austausch von Chlor, Brom, und Jod zwischen organischen und anorganischen Halogenverbindungen. *Inaug. Diss.*, Tübingen, 1885; *Liebig's Annalen*, **231**, 257.

87.—Conrad Kerez. Ueber die Einwirkung von Halogenverbindungen des Aluminiums auf Halogensubstituirte Kohlenwasserstoffe. *Inaug. Diss.*, Tübingen, 1885; *Liebig's Annalen*, **231**, 285.

88.—Ad. Römer. Untersuchungen über den Einfluss der Masse auf die Chlorirung brennbarer Gase. *Inaug. Diss.*, Tübingen, 1885. *Liebig's Annalen*, **233**, 172.

1886. 89.—Ueber die Verbrennung von Kohlenoxyd. *Ber.*, **19**, 1099.

90.—Jul. Giersbach. Ueber die Nitrirung des Benzol. *Inaug. Diss.*, Tübingen, 1886.

91.—Emil Meyer. Ueber die Affinität der Vitriolmetalle zum Wasser. *Inaug. Diss.*, Tübingen, 1886.

1887. 92.—Die bisherige Entwickelung der Affinitätslehre. *Zeit. physikal. Chem.*, **1**, 134; also *Phil. Mag.*, **23**, 504.

93.—Ueber die Einwirkung von Chlorkohlenstoff auf Oxyde. *Ber.*, **20**, 681.

94.—Apparat zur fractionirten Destillation unter verminderten Drucke. *Ber.*, **20**, 1833.

95.—Ueber Sauerstoffüberträger. *Ber.*, **20**, 3058.

96.—Ueber die Darstellung von Jodwasserstoff. *Ber.*, **20**, 3381.

97.—Ueber die Constitution des Benzols. *Liebig's Annalen*, **247**.

98.—Arth. Kessler. Die Nitrirung des Benzols in ihrer Abhängigkeit von der Masse der wirkenden Stoffe. *Gekrönte Preisarbeit und Inaug. Diss.*, Tübingen, 1887.

1887. 99.—Jul. Eisenlohr. Ueber Nitro- und Bromnitroderivate des Phenols. *Inaug. Diss.*, Tübingen, 1887.

100.—Friedr. Neubeck. Ueber Molekularvolumina aromatischer Verbindungen. *Inaug. Diss.*, Tübingen, 1887; *Zeit. physikal. Chem.*, **1**, 649.

101.—Rich. Fink. Ueber die Affinität der Vitriolmetalle zur Schwefelsäure. *Inaug. Diss.*, Freiburg, 1 B., 1888; *Ber.*, **20**, 2106.

102.—Fr. Binnecker. Ueber verschiedene Metallsalze als Sauerstoffüberträger an schweflige Säure. *Inaug. Diss.*, Tübingen, 1887.

1888. 103.—Ueber die Nitrirung des Benzols. *Zeit. physikal. Chem.*, **2**, 676.

104.—Osc. Burchard. Ueber die Oxydation des Jodwasserstoffes durch die Sauerstoffsäuren der Salzbilder. *Inaug. Diss.*, Tübingen, 1888; *Zeit. physikal. Chem.*, **2**, 796.

105.—Ernst Schürmann. Ueber die Verwandtschaft der Schwermetalle zum Schwefel. *Inaug. Diss.*, Tübingen, 1888; *Liebig's Annalen*, **249**, 326.

106.—Ad. Mente. Ueber einige anorganische Amide. *Inaug. Diss.*, Tübingen, 1888; *Liebig's Annalen*, **247**, 232.

107.—Alb. Bonz. Ueber die Bildung von Amid aus Ester und Ammoniak und die Umkehrung dieser Reaction. *Inaug. Diss.*, Tübingen, 1888; *Zeit. physikal. Chem.*, **2**, 865.

1889. 108.—Ueber Nitrirung. *Ber.*, **22**, 18.

109.—Ueber Salpetersäureanhydride. *Ber.*, **22**, 23.

110.—Ueber die Umsetzung von Säureamiden mit Alkoholen. *Ber.*, **22**, 24.

111.—Nachträgliches über Luftbäder. *Ber.*, **22**, 879.

112.—Ueber Gasheizung. *Ber.*, **22**, 883.

113.—L. M. und Karl Seubert. Die Einheit der Atomgewichte. *Ber.*, **22**, 872 and 1161, 1392.

114.—Phil. Löhr. Ueber die Einwirkung von Alkyljodiden auf Cadmium und Magnesium. *Inaug. Diss.*, Tübingen, 1889; *Liebig's Annalen*, **241**, 48.

115.—Sigm. Feitler. Ueber die Molekularvolumina einiger Substitutionsproducte aromatischer Kohlenwasserstoffe. *Inaug. Diss.*, Tübingen, 1889; *Zeit. physikal. Chem.*, **4**, 66.

1890. 116.—Ueber das Wesen des osmotischen Druckes. *Zeit. physikal. Chem.*, **5**, 23.

117.—Heinr. Fulda. Ueber die Sulfurirung des Chinolins und des Phenols. *Inaug. Diss.*, Tübingen, 1890; *Zeit. physikal. Chem.*, **6**, 190.

1891. 118.—Zur Theorie der Lösungen. *Sitzungsber. d. K. Preuss. Akad. d. Wissensch. zu Berlin*, 1891, **48**, 993.

119.—Wm. McKerrow. Zur Kenntniss der Bromüberträger. *Inaug. Diss.*, Tübingen, 1891; *Ber.*, **24**, 2939.

120.—W. Pullinger. Ueber Platin-Kohlenoxydverbindungen. *Ber.*, **24**, 2291.

121.—L. M. und Karl Seubert Die Einheit der Atomgewichte. *Pharm. Rundschau*, New York, 1891, **9**, No. 4.

1892. 122.—Ueber den sogenannten osmotischen Druck. *Wied. Annalen*, **46**, 166.

123.—John A. Harker. Ueber den Umsatz von Wasserstoff mit Chlor und Sauerstoff. *Inaug. Diss.*, Tübingen, 1892; *Zeit. physikal. Chem.*, **9**, 673.

124.—Walter Lippert. Ueber die Zersetzung der Aether durch Wasserstoff-

säuren. *Inaug. Diss.*, Tübingen, 1892; *Zeit. physikal. Chem.*, **276**, 148.

1892. 125.—Herm. Flech. Ueber Magnesium Alkyle. *Inaug. Diss.*, Tübingen, 1892; *Liebig's Annalen*, **276**, 129.

1893. 126.—Ein kleines Labatoriumluftthermometer. *Ber.*, **26**, 1047.

127.—Ueber den Vortrag der anorganischen Chemie nach dem natürlichen System der Elemente. *Ber.*, **26**, 1230.

128.—Ueber die Köhnlein'sche Darstellung der Paraffine. *Ber.*, **26**, 2070.

129.—Nachtrag zu der Abhandlung von A. Weigle. *Zeit. physikal. Chem.*, **11**, 426.

130.—A. Weigle. Spectrophotometrische Untersuchung der Salze aromatischer Basen. *Inaug. Diss.*, Tübingen, 1896; *Zeit. physikal. Chem.*, **11**, 227.

131.—John C. Cain. Ueber die Einwirkung von Chlorwasserstoffsäure auf Aethylalkohol. *Inaug. Diss.*, Tübingen, 1893; *Zeit. physikal. Chem.*, **12**, 751.

132.—Rich. Theurer. Einwirkung von Salzsäure auf einige Triphenylmethan-Farbstoffe. *Inaug. Diss.*, Tübingen, 1893.

1894. 133.—Electrolyse der Salzsäure als Vorlesungsversuch. *Ber.*, **27**, 850.

134.—Ueber Acetylen, eine Warnung. *Ber.*, **27**, 2766.

135.—Ueber die Darstellung der Paraffine. *Ber.*, **27**, 2766.

136.—Die niederen Paraffine. Aethan und Propan. *Ber.*, **27**, 2767.

137.—Ein Trockenschränkchen aus Aluminium. *Ber.*, **27**, 7769.

138.—L. M. und Karl Seubert. Ueber das Verhältniss der Atomgewichte des Wasserstoffs und Sauerstoffs. *Ber.*, **27**, 2770.

139.—Fritz Klunge. Zur Köhlenlein'schen Darstellung der Paraffine. *Inaug. Diss.*, Tübingen, 1894; *Liebig's Annalen*, **282**, 214.

140.—Ad. Hainlen. Ueber Propan und Aethan in flüssigem Zustande. *Inaug. Diss.*, Tübingen, 1894; *Liebig's Annalen*, **282**, 229.

141.—C. Haacke. Spektrophotometrische Untersuchungen über die Einwirkung von Salzsäure auf einige Substitutionsproducte des Fuchsins. *Inaug. Diss.*, Tübingen, 1894.

142.—Fritz Woga. Ueber Magnesium-Diphenyl. *Inaug. Diss.*, Tübingen, 1894. *Liebig's Annalen*, **282**, 320.

1895. 143.—Die Constitution der Fuchsine. *Ber.*, **28**, 519.

144.—Otto Degner. Ueber Isobutan, normales Butan, und Propylen in flüssigem Zustande. *Inaug. Diss.*, Tübingen, 1895.

145.—Wilh. Ludwig. Ueber gegenseitige Löslichkeit einiger nicht mischbaren Flüssigkeiten. *Gekrönte Preisarbeit*, Tübingen, 1895.

146.—E. Manz. Ueber einige Aether des Triphenylmethans und Trinitrotriphenylmethans. *Inaug. Diss.*

III. *Miscellaneous Articles.*

147.—Zur Erinnerung an Leopold von Pebal. Nekrolog. *Ber.*, 1887, **20**, R., 997.

148.—Eugen Lellmann. Nekrolog. *Ber.*, 1893, **26**, R., 1033.

149.—Die Chemie in ihrer Anwendung auf Forstwirthschaft. *Zeit. f. Forst- und Jagdwesen*, 1867, **3**, 312.

150.—Ueber die neuere Entwickelung der chemischen Atomlehre. Vortrag gehalten zu Plochingen, 25 January, 1885. *Böklen's Math.-naturw. Mitth.*, **3**, 24 pp.

1895. 151.—Ueber den Vortrag der anorganischen Chemie nach dem natürlichen System der Elemente. Vortrag gehalten in der deutschen chemischen Gesellschaft zu Berlin, 29 Mai, 1893. *Ber.*, **26**, 1230.

152.—Ueber naturwissenschaftliche Weltanschauung. Rede am Geburtsfeste S. M. des Königs gehalten vom derzeitigen Rektor L. M. 27 February, 1895. Tübingen.

153.—"Allotropy." Article for *Watt's Dictionary*, 1885, **1**, 128—131.

154.—Kritiken und Bücheranzeigen. *Zeit. f. Chem. Jahrg.*, 1865—1868.

Articles on Education.

155.—Die Zukunst der deutschen Hochschulen und ihrer Vorbildungsanstalten. Breslau. Maruschke and Berendt, 1873.

156.—Akademie oder Universität? Den deutschen Forst- und Land-wirthen gewidmet. Breslau. Maruschke and Berendt, 1874.

157.—Ueber akademische Lernfreiheit. Vortrag in der Dienstags-Gesellschaft zu Tübingen, 25 Februar, 1879. *Nord und Süd, Jahrg.*, 1879.

158.—Ueber die gewerbliche Schulfrage, Verhandl. d. Centralverb. D Industr. Versamml. in Nürnberg, 18 September, 1882. *Ber.*, S. 98.

159.—Mathematik und Naturwissenschaften in der Einheitsschule. *Schriften des D. Einheitsschulvereins*, Heft 1, 1887.

160.—Die Reform der höheren Schulen. Daselbst, Heft 6, 1890.

181.—Wünsche für den mathematischen und naturwissenschaftlichen Unterricht an Gymnasien. *Uhlig's Zeitschr. Das humanistische Gymnasium.* Jahrg. 1.

162.—Die Vorbildung der Studirenden. *Nord und Süd*, **58**, *Heft* 172, 57.

PASTEUR MEMORIAL LECTURE.*

(Delivered on March 25th, 1897)

By Percy Frankland, Ph.D., B.Sc., F.R.S.,† Professor of Chemistry in Mason College, Birmingham.

We are assembled here this evening for the purpose of publicly calling to mind and recording some of the great achievements of a man whose master mind has not only exerted a wonderful influence on the development of several sciences, but whose successful labours are closely interwoven with much of the progress which has taken place in many departments of practical life during the latter half of this century.

Although the name of Pasteur belongs to so many branches of science, I would claim his glory for our own, as I believe his phenomenal success in such varied fields of investigation to be in large measure due to his having been reared under that chemical discipline in which we place our faith, and in his having, almost for the first time, extended the experimental methods and close reasoning of the chemist to other sciences in which, hitherto, investigators had been mostly busied with matters of superficial description and empty nomenclature.

Of the intellectual development of this great master of the experimental method we are fortunately very fully informed, as not only are we in possession of what is practically an autobiography from the pen of his son-in-law, but some of his coadjutors, who were in daily association with him during the most active years of his life, have furnished personal reminiscences of the progress of his mind through those varied fields in which he laboured so arduously and so well.

In a poor quarter of Dôle stands a little house bearing the simple inscription in gold :

"Ici est né Louis Pasteur
le 27 Décembre, 1822."

When an infant of but two years of age, his parents removed to the town of Arbois, where his childhood was passed, for here his father purchased a small tannery. That this hard-working tanner was a man of character and stern experience is shown by the fact that he had fought in the legions of the First Empire, and that he had been decorated on the field of battle by Napoleon, but the rough soldier had

* Chemical Society's Memorial Lecture, No. VI.

† I am indebted for the excellent portrait of M. Pasteur to his son-in-law, M. R. Vallery-Radot.

his heart in the right place, and the home at Arbois appears to have been one of those establishments which revolve round the children, and the greatest sacrifices were made by the parents to secure the best educational advantages for the son. Nor was Pasteur unmindful of this unselfish devotion in after years, for the most celebrated of his works* bears the dedication :

"*á la Mémoiré de mon Père*"
"*ancien militaire sous le Premier Empire, Chevalier de la Légion d'Honneur,*'

a tribute surely more imperishable and more covetable even than the ribbon pinned to his tunic by the victor of Marengo and Austerlitz !

At the Collège Communal, which Pasteur attended at Arbois, he did not for some time evince any interest in books or study, but found his pleasure in fishing and in drawing portraits of his companions and neighbours, for he possessed already, at this early age, marked ability as a draftsman, a gift which must have stood him in good stead on many occasions in after life.

As soon, however, as Pasteur realised the strain upon the resources of his parents which his education entailed, he threw off his lethargy, locked away his cherished pastels so as to be delivered from temptation, and rapidly developed that passion and enthusiasm for work which ultimately dominated his life, and which the greatest vicissitudes proved powerless to break.

The College at Arbois having no chair of philosophy, Pasteur proceeded to Besançon, where he graduated Bachelier ès Lettres, and was at once appointed 'maître répétiteur' in the college. The fond ambition and hope of his father was often repeated :—"Ah ! ci tu pouvais devenir un jour professeur, et professeur au collège d'Arbois, je serais l'homme le plus heureux de la terre." But his old schoolmaster had already formed a juster estimate of young Pasteur's powers, saying, "Ce n'est pas vers la chaire d'un petit collège comme le nôtre qu'il faut le diriger, il faut qu'il soit professeur dans un collège royal . . . Mon petit ami, pensez à la grande École normale !"

Pasteur's interest in chemical science had already begun at this time, and we are told how he was in the habit of embarrassing the venerable Professor Darlay with difficult questions in the presence of his class. I think it may be taken as a very safe generalisation that the real attainments of a man are in direct proportion to the frequency of his use of the words, "I don't know," and judged by this rule, the knowledge of this aged professor of physics and chemistry at Besançon must have been limited indeed, as he tried to safeguard his dignity by telling his pupil that it was for him to interrogate Pasteur, and not for Pasteur to catechise him before all his scholars. Checked in his

* *Études sur la Bière*, 1876.

enquiries in this direction, Pasteur endeavoured to satisfy his craving for chemical knowledge by seeking assistance from a pharmacist who enjoyed considerable local reputation through being the author of a paper which had been deemed worthy of publication in the *Annales de Chemie et de Physique*.

An incident attended Pasteur's entry as a student at the École normale which is worth recording as indicative of his extraordinary perseverance, and of the exacting standard of performance which he imposed upon himself. Having presented himself for the entrance examination, he duly passed, but only obtaining the fourteenth place, he withdrew for further preparation, and in the following year, in October, 1843, obtained the fourth place.

Once admitted within the magic portals of this great temple of learning, Pasteur found full scope for gratifying his taste for chemistry, which had been rapidly ripening during the past few years. As a student at the École normale, he enjoyed the privilege of attending the lectures both of Balard at the École normale, and of Dumas at the Sorbonne. By each of these great masters of our science, the young Pasteur was impressed by what was most admirable, by the great grasp of well digested facts and details possessed by the discoverer of bromine, by the lofty generalisations indulged in by the author of the theory of types.

Not even on Sundays did Pasteur rest from his chemical studies, and we as chemists can perhaps best form some idea of his boundless energy by the fact that, on one of these days of rest, he actually succeeded in preparing no less than 60 grams of phosphorus from bones, the operation lasting from four in the morning to nine o'clock at night.

It is, doubtless, the experience of many who have attended great seats of learning, that whatever may be the indebtedness to professors, the real fire of research is not unfrequently kindled by the fertile suggestions of junior men with whom students can associate on more equal terms, and although Pasteur may have owed much to Dumas and Balard, there can be no doubt that he was helped on to the first rung of the ladder which he scaled with such dexterity and success by a man of this kind. It was M. Delafosse, a former pupil and assistant of the renowned Haüy, who turned Pasteur's attention to the study of crystals and to problems of molecular physics, in which domain his first, and I venture to think his most evergreen, laurels were won.

It is not uncommon to hear regrets expressed at the difficulty of finding subjects for research, but even at the present day wherever the frontier line between the known and the unknown be examined, a point will be found where the zealous investigator can add some new territory to that fair dominion which man has wrested from the vast

continent of darkness with which he has been surrounded by the Creator. If that is so to-day, how much more must it have been the case 50 years ago, when Pasteur was first impelled to enlist for active service in the ranks of science. A few words will suffice to indicate the antecedents which led to Pasteur being drawn into the particular field of research in which so many of his qualities were for the first time revealed to the world.

As you are aware, the phemonena of double refraction were already known to Huygens and Newton, but the subtle nature of the light composing the ordinary and extraordinary rays respectively was not understood until Malus, in 1808, made the far-reaching discovery of the polarisation of light by reflection, and subsequently showed that the rays which are transmitted through Iceland spar differ from ordinary light in being polarised.

The wonderful and intricate phenomena of polarisation, which form such an attractive chapter in experimental optics, were investigated after the untimely death of Malus, in 1812, by Arago, and more especially by Biot, who practically devoted his whole life to this study. It is almost impossible to overestimate the debt which chemists owe to the patient researches of this physicist, for in the course of his labours he made, in 1815, the discovery that there are a number of natural organic substances, such as sugar, camphor, tartaric acid, oil of turpentine, &c., which possess the remarkable property of rotating the plane of polarisation, either in the liquid or dissolved state. Nor was Biot slow in perceiving the enormous theoretical importance of this discovery, for he at once pointed out that, whereas in the previously known phenomena of the rotation of the plane of polarisation by crystals such as quartz the rotation is conditioned by the crystalline form, disappearing altogether as soon as that form is destroyed, on the other hand, in the case of these organic substances this rotatory power must be inherent in the molecules themselves, for being exhibited by liquids it must be dependent on the one structure which still remains—the molecule itself. This discovery of Biot's had thus placed the physical phenomena of polarisation on the door-step of the chemist; and we shall soon see how the latter has availed himself of this unexpected legacy.

Other physical phenomena, however, were about this time being turned to advantage by chemists, and of these perhaps the most notable was the striking property of isomorphism, leading as it did, in the able hands of Mitscherlich, to those important deductions and generalisations with which we are so familiar. It was these phenomena of isomorphism that accidentally led to the utilisation of Biot's bequest, and started Pasteur on that great voyage of discovery which was coextensive with his life.

In 1884, M. Biot communicated to the Academy of Sciences a note by Mitscherlich, in which the German mineralogist expresses himself as follows (*Compt. rend.*, 1844, **19**, 720).

"The paratartrate (racemate) and the tartrate of soda and ammonia (double salt) have the same chemical composition, the same crystalline form, with the same angles, the same specific gravity, the same double refraction, and therefore the same angles between their optical axes. Their aqueous solutions have the same refraction. But the solution of the tartrate rotates the plane of polarisation, whilst the paratartrate is inactive, just as M. Biot has found to be the case for the whole series of these two kinds of salts; but here the nature and the number of the atoms, their arrangement and their distances, are the same in the two bodies submitted to comparison."

Pasteur had now completed his curriculum at the Ecole normale, and he was at once retained as assistant by his former master, M. Balard. Having now the opportunity of carrying on research, all other matters appeared to him of subsidiary importance. He realised, indeed, that his training was yet far from complete, and in order to perfect himself in crystallography, with which study he had become enamoured through his inspiring intercourse with Delafosse, he determined to repeat a very complete piece of work by M. de la Provostaye on the crystalline form of the tartrates. It was soon evident, however, that mere repetition and confirmation were not Pasteur's strong points, for although a comparative novice at the kind of work in question, he was able to see what had escaped the observation of his skilled predecessor in this field. Thus, both on the crystals of tartaric acid itself, as well as on those of its salts, he at once found small facets which had not hitherto been described.

The presence of such facets on crystals of quartz had not escaped the attention of Haüy, who indeed had further divided such quartz crystals into left and right-handed quartz, according to the side on which these facets were developed. Biot, again, in his extended investigations on polarisation, had found that some specimens of quartz turn the plane of polarisation to the right and some to the left, whilst Sir John Herschell, in 1820, suggested that the two phenomena were connected, and that the left-handed quartz crystals rotated the plane of polarisation in one direction, the right-handed in the other. Experiment showed that this was actually the case. These remarkable relations appear to have made a profound impression on young Pasteur, and so deeply imbued was he with the idea that polarimetric effect must be associated with crystalline form, that the appearance of these hemihedral faces (as these facets are technically called) seemed to him of the very highest importance, and to deserve the most careful study. To this end, he prepared no less than 19 different tartrates, and found that all exhibited hemihedral faces.

He found, however, much more than this, for he discovered that the hemihedral faces were similarly situated in all these tartrates, and that the solutions of all of them rotated the plane of polarisation in the same direction. Pasteur's natural inference was that hemihedral form and rotatory power were similarly linked together in the case of these tartrates as they were already known to be in the case of quartz, notwithstanding the fundamental difference between the rotation phenomena exhibited by the quartz and the tartrates respectively, namely, that the quartz only possesses the power in the crystallised state, the tartrates in solution.

Now Pasteur, although always ready with an hypothesis, valued such hypotheses only as a stimulus and guide to further experimental research. He proceeded, therefore, not only to examine the crystals of other optically active bodies, but, recognising that Mitscherlich's statement given above was absolutely incompatible with the hypothesis of the relationship between optical activity and hemihedrism which had forced itself upon him, he set about also examining the crystalline form of racemic acid and its salt, the inactivity of which to the polarised beam had already been demonstrated by Biot. In accordance with his anticipations, based upon his hypothesis, he found that the crystals of the racemates exhibited no hemihedral faces at all.

The divinity that shapes our ends had, however, not only endowed Pasteur with numerous faculties of a very high order, but had decreed also that he should be favoured with the most extraordinary luck; indeed I am disposed to think that most men who have achieved a great reputation have been similarly dealt with, and it is the indebtedness which many of them have felt to chance which has so often inclined them to belief in fate and destiny.

Now Mitscherlich had made his allegation with respect to a particular racemate, namely, the sodium ammonium salt, and Pasteur, therefore, naturally specially examined this. On preparing it, to his intense surprise, and quite contrary to the anticipations of his hypothesis, he found that the hemihedral faces were indeed there. But on examining them more closely, he saw that, whilst in the tartrate the facets were all turned towards the right, in some of these racemate crystals they were turned to the right, and in others turned to the left. Still obeying the promptings of his hypothesis, he sedulously picked out the right-handed crystals and placed them in one heap, and the left-handed crystals in another, dissolved each group of crystals in water, and then examined the two solutions separately in the polarimeter—with what results we all know, for it is one of the most classical experiments in the whole range of chemical science; the solution of the right-handed crystals turned the plane of polarisation to the right, the solution of the left-handed crystals to the left. Looking back upon

this experiment after 50 years, and with the knowledge of what has followed from it, we cannot fail to be struck with the dramatic nature of the situation; nor is it difficult to realise the intense excitement which it must have caused the young investigator. Indeed, fortunately, the scene has been handed down, and it appears that on obtaining this result Pasteur was so overcome with excitement that he at once rushed from the laboratory, and meeting M. Bertrand, embraced him, exclaiming:

"Je viens de faire une grande découverte! J'ai séparé le paratartrate double de soude et d'ammoniaque en deux sels de dissymétrie inverse et d'action inverse sur le plan de polarisation de la lumière. Le sel droit est de tout point identique au tartrate droit. J'en suis si heureux que j'éprouve un tremblement nerveux qui m'empêche de remettre de nouveau l'œil à l'appareil de polarisation."

Thus chance, which had led him to examine this comparatively obscure double salt of racemic acid, afforded him the opportunity of making this brilliant discovery, which has proved of such priceless value to chemical science.

It was only natural that the communication of these most remarkable results should have caused the liveliest interest at the Academy of Sciences; we are, however, quite familiar with remarkable results obtained by mature and well-seasoned investigators being received with incredulity or reserve, as it is euphemistically called, and it is not surprising, therefore, that such a striking discovery made by a young and almost unknown man should have been accepted with considerable hesitation. The duty of reporting on this paper was entrusted to the highest living authority on such a subject, to M. Biot himself, and I am tempted to give you Pasteur's own account of the extraordinarily stringent investigation to which the half-sceptical veteran submitted the young man's almost suspiciously plausible results:

"He (M. Biot) sent for me to repeat before his eyes the several experiments. He gave me racemic acid which he had himself previously examined and found to be quite inactive to polarised light. I prepared from it in his presence the sodium ammonium double-salt, for which he also desired himself to provide the soda and ammonia. The liquid was set aside for slow evaporation in one of the rooms of his own laboratory, and when 30—40 grams of crystals had separated he again summoned me to the Collège de France, so that I might collect the dextro- and lævo-rotatory crystals before his eyes, and separate them according to their crystallographic character, asking me to repeat the statement that the crystals which I should place on his right hand would cause deviation to the right, and the others to the left. This done, he said that he himself would do the rest. He prepared the carefully weighed solutions, and, at the moment when he was about to examine them in the polarimeter, he again called me into his laboratory. He first put the more

interesting solution, which was to cause rotation to the left, into the apparatus. Without making a reading, but already at the first sight of the colour-tints presented by the two halves of the field in the Soleil saccharimeter, he recognised that there was a strong lævo-rotation. Then the illustrious old man, who was visibly moved, seized me by the hand, and said, 'Mon cher enfant, j'ai tant aimé les sciences dans ma vie que cela me fait battre le cœur!'"

But to return to Pasteur's discovery of the possibility of resolving racemic acid, by crystallising the sodium ammonium salt, into equal proportions of the well known dextro-tartaric acid, identical with the well known acid of grape juice on the one hand, and of the hitherto unknown lævo-tartaric acid on the other.

He proceeded to show how these two acids and their salts were related to each other in a manner so far unknown for any other substances. The two acids he found to be identical in every particular; their crystals presented the same forms, the same faces, the same angles, the same hemihedrism, the only difference between them consisting in the right- and left-handed *disposition* of their hemihedral faces, and in the right- and left-handed directions of their equal rotatory powers.

Not only, however, did he show that racemic acid can be thus split into equal proportions of dextro- and lævo-tartaric acids, but he demonstrated that these two acids could be again made to yield racemic acid; by taking somewhat concentrated solutions of the two acids in equivalent proportions and mixing them, he obtained an abundant separation of the crystals of racemic acid, in every respect identical with the natural product, and the process being accompanied by evolution of heat, he concluded that it was a real chemical combination, and not mere mechanical mixture (see, in this connection, Ladenberg *Ber.*, 1897, **30**, 485).

Whilst this investigation reveals the extraordinary powers of observation and experimental skill with which Pasteur was endowed, the conclusions which he drew from the results he had obtained serve to display the acumen of his reasoning, the clearness of his mind, and his immediate appreciation of the ultimate significance of facts. Thus the philosophical reflections in which he indulges over this discovery show how so long ago he had completely foreshadowed and grasped the scope of that important branch of our science which we now call *Stereochemistry*, and which, even many years later, was regarded as chimerical by those who had either lost the elasticity of youth or had never possessed it.

Thus how admirable is the courage, the prophetic insight, and the self control with which he expresses himself on the bearings of his discovery.

(Two lectures on *Asymmetry in Natural Organic Compounds*, delivered before the Chemical Society of Paris on Jan. 20th and Feb. 3rd, 1860).

"In isomeric bodies the elements and the proportions in which they are combined together are the same, the arrangement of the atoms is alone different. The great interest attaching to isomerism lies in the introduction of the principle that bodies can be and really are distinct through possessing different arrangements of their atoms within their molecules.

"But there were no isomeric bodies for which the relationship existing between their molecular arrangements was known. This gap is for the first time filled up by the discovery of the constitution of racemic acid, and of the mutual relations subsisting between dextro- and lævo-tartaric acid. We know, on the one hand, that the molecular arrangements of the two tartaric acids are asymmetric, and, on the other hand, that these arrangements are absolutely identical, excepting that they exhibit asymmetry in opposite directions. Are the atoms of the dextro-acid grouped in the form of a right-handed spiral, or are they placed at the apex of an irregular tetrahedron, or are they disposed according to this or that asymmetric arrangement? We do not know. But there can be no doubt that we are dealing with asymmetric arrangements which are not superposable. It is equally certain that the atoms of the lævo-acid are disposed in an exactly opposite manner. Finally, we know that racemic acid is formed by the union of these two groups of oppositely arranged asymmetric atoms.

"From now onwards the knowledge of the chemical and physical analogies and differences corresponding with these arrangements, the relationship between which has been ascertained, acquires a particular interest, and provides a sure foundation for molecular mechanics. It enables us to determine the relationship between physical and chemical properties and molecular arrangement, which conditions these very properties, and, *vice versâ*, it permits us to draw conclusions from these very properties with regard to their first cause. These general relations between properties and corresponding arrangements may be thus summarised:—

"1. When the atoms of organic compounds are asymmetrically arranged, this molecular asymmetry is betrayed by the crystalline form exhibiting non-superposable hemihedrism.

"2. The presence of this molecular asymmetry reveals itself by optical rotatory power.

"The cause of this rotatory power is thus also ascertained.

"3. When this non-superposable molecular asymmetry appears in two opposed forms, as in the case of dextro- and lævo-tartaric acids and all their derivatives, then the chemical properties of these identical but optically opposite bodies are exactly the same, from which it follows that this type of contrast and analogy does not interfere with the ordinary play of the chemical affinities."

These words were spoken by Pasteur more than 37 years ago, yet such is their freshness and permanence, that there is hardly a statement which they make requiring modification to-day, and they set

forth in the clearest possible manner the guiding principles of that branch of our science which his genius has created.

One error which indeed pervades the above passage must be pointed out, and that is the supposed necessity that molecular dissymmetry should be betrayed by dissymmetric crystalline form. Indeed, Pasteur himself discovered that this relationship did not hold good, but it was a feature of his genius that his very mistakes proved fertile, and led to the establishment of important truths. Thus the whole of his investigation on the tartrates had been suggested and guided by this preconceived idea that molecular dissymmetry must invariably receive expression both in rotatory power and in dissymmetry of crystalline form. (It will be shown later, that there is at present a tendency amongst crystallographers to revert to Pasteur's original opinion in this matter, as many crystals, externally destitute of asymmetry, can be made to display it by artificial treatment.)

But if we are impressed with the sagacity and suggestiveness of Pasteur's theoretical speculations, we are filled with even still greater admiration on again turning to his experimental work. The field of investigation which he exposed to view by his discovery of the relationship between the racemic and tartaric acids appears as limitless as the prairie which is bounded only by the horizon; this domain has in recent years engaged the attention of an ever increasing number of workers, and nothing can testify more eloquently to the experimental genius of Pasteur than the circumstance that already, during the comparatively short period of time that he himself was pursuing its cultivation, he succeeded in determining the exact methods by means of which it can be exploited. No new methods have been devised, no substantial modifications or improvements have been introduced, the machinery which he designed for its tillage is still exclusively in vogue, although the estate which he abandoned nearly 30 years ago has been subdivided, and has passed into many hands of divers nationalities.

I need hardly remind you of the nature of that machinery designed by Pasteur for the preparation and transformation of physical isomers. His original method for the separation of the oppositely active components of an inactive racemate was, as we have seen, by the crystallisation of a particular compound resulting in the formation of crystals of the two individual components which were then separated by means of their hemihedral faces. This obviously laborious method was slightly modified by Gernez, who obtained the resolution of the racemate by introducing into its supersaturated solution a crystal of one of its active components, a proceeding which is sometimes attended by the crystallisation of that component, so that it can be separated from the opposite component which remains dissolved.

This method, which is of peculiar interest theoretically, has only in

comparatively rare instances been found available for the decomposition of racemoids, and the good fortune which Pasteur had in coming upon it before all others is the more extraordinary.

The feat of decomposing racemoid bodies has, so far as I am aware, been accomplished by this method only in some half-dozen other different cases, perhaps the most notable of these being the resolution of ordinary lactic acid into its active components by means of the zinc ammonium salt, in a solution of which a nucleus of one of the active components is employed to induce the crystallisation of this active component from the inactive racemoid. This ingenious application of the Pasteur-Gernez method is due to my friend and former colleague, Prof. Purdie (Trans., 1893, 63, 1143), of St. Andrews', who is known to every reader of our Journal as one of the most indefatigable workers in the field of stereochemistry in this country. In the case of inactive asparagine, again, it has been shown that crystallisation always takes place as a mixture of enantiomorphic forms, so that possibly in this case a true racemoid does not exist at all; and again, it has been shown by Emil Fischer (*Ber.*, 1892, 25, 1025) that an inactive solution of *d*- and *l*-gulonic lactones deposits a mixture of the two isomerides, although some of the inactive derivatives made from such a mixture crystallise as true racemoids.

I may also refer, in passing, to the fact that it has been shown by Van't Hoff (*Ber.*, 1886, 19, 2142) that this decomposition of racemoids by crystallisation is of great interest in connection with problems of chemical equilibrium (see also Winther, "Zur Theorie der Spaltungen der racemischen Formen," *Ber.*, 1895, 28, 3000).

Pasteur has, however, given us another method of effecting the fission of the racemoids into their optically active components, and whilst he was led to the first method by pure chance, the second was arrived at as the result of theoretical speculations concerning this conception of dissymmetry which he had introduced into chemical science, and which has proved of such remarkable fertility. I cannot do better than give you his own account (*Lectures on Asymmetry*, 1860) of the reasoning which he employed, as you may not possibly all be aware of how fully conversant he was already, forty years ago, with the problems which to some appear almost premature to-day:

"All chemical compounds, whether natural or artificial, whether mineral or organic, must fall into one of two classes; symmetrical compounds with superposable mirror-image and asymmetrical compounds with non-superposable mirror-image.

"This being the case, the properties of the two tartaric acids and their derivatives remain identical as long as they are brought into contact with bodies of the first class, for example, with potash, soda, ammonia, lime, baryta, aniline, alcohol, the ethers, in short with all bodies devoid of asymmetry, devoid of hemihedrism, and without action on polarised light.

"On the contrary, if they are subjected to the action of bodies of the second class, such as asparagine, quinine, strychnine, brucine, albumin, sugar, &c., or of other asymmetric bodies like themselves, then totally distinct phenomena make their appearance. The solubility is different. If combination takes place, then the products differ from each other in crystalline form, in specific gravity, in the amount of water of crystallisation, in stability on heating, in fact just in the same way as the most distantly related isomers can differ from each other.

"Thus the molecular asymmetry of bodies appears as an important agent for the alteration of affinities. Towards the two tartaric acids quinine does not behave like potash, and only for the reason that it is asymmetric and that potash is not. Asymmetry, as already stated, exhibits itself in this case as a property which is in itself capable of altering the chemical affinities. I do not think that any previous discovery has penetrated so deeply into the mechanics of the problem of the genesis of chemical compounds.

"Let us endeavour to illustrate these points of similarity and dissimilarity by means of a picture. Imagine a right-handed and a left-handed screw, each driven into a separate but identical block of wood possessing a rectilinear fibre. All the mechanical conditions of the two systems will be the same; but this will cease to be the case as soon as the same screws penetrate into blocks which are themselves of either right- or left-handed spiral structure.

"The knowledge that salts of dextro- and lævo-tartaric acid can only become possessed of such different properties through the optical activity of the base with which they combine, justified the hope that this difference itself might be caused by chemical forces which were capable of counteracting the mutual affinity of the two acids, and which would thus afford a means of splitting racemic acid into its components. Many are the abortive attempts which I have made in this direction, but I have at length achieved success with the assistance of two new isomeric bases, quinicine and cinchonicine, which I can very easily obtain from quinine and cinchonine (*Jahresber.*, 1853, 473) respectively.

"I prepare the cinchonicine racemate by first neutralising the base and then adding as much acid again. The first crystals to separate are perfectly pure cinchonicine lævotartrate. The whole of the dextrotartrate remains in the mother liquour, as it is more soluble; gradually this also crystallises out, but in forms which are totally distinct from those of the lævotartrate. It might be supposed, indeed, that one was dealing with two entirely different salts of unequal solubility."

Whilst Pasteur's first method of decomposing racemoids has proved, as we have seen, chiefly of theoretical interest, and has been practically used for the resolution of racemoids in only a few instances, his second method, depending on the interaction of the racemoid with an optically active molecule with the result that the two compounds formed from the enantiomorphic components of the racemoid differ so widely in respect of solubility as to admit of their separation, has, on the other hand, been most successfully employed by a number of chemists, and has proved the master key to some of the most remarkable organic syntheses which have hitherto been realised.

The method admits obviously of twofold application; first, for the resolution of racemoid acids by means of optically active bases, such as the natural alkaloids; and, second, for the resolution of racemoid bases by means of optically active acids, such as tartaric acid. It would be impossible for me even to enumerate the racemoids which, by the application of this principle, have been made to yield up their enantiomorphic constituents, and I will, therefore, confine myself to citing the two principal series of investigations in which the utilisation of this second method of Pasteur's has led to the most striking results.

In the whole range of organic chemistry there are probably no researches which have excited wider interest, and called forth more general admiration, than those which have resulted in the artificial synthesis of natural alkaloids by Ladenburg, and those which have culminated in the laboratory-made sugars of Emil Fischer. Both of these great achievements have largely depended on the successful application of Pasteur's second method of racemoid fission.

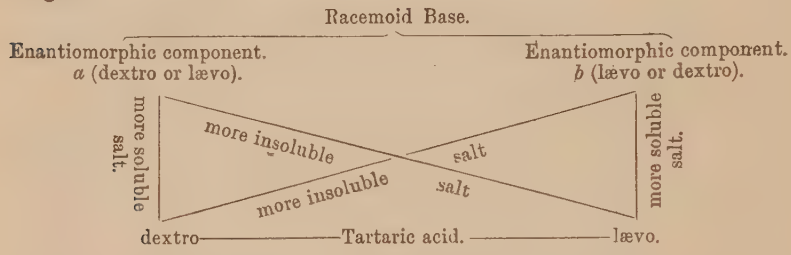
Ladenburg's synthetic coniine was of necessity a racemoid destitute of optical activity, and thus lacked the last attribute necessary to render it identical with the natural alkaloid present in hemlock, but by converting the inactive artificial product into the acid tartrate, a coniine tartrate was crystallised out from which the active base, *d*-coniine, identical in every particular with the natural alkaloid, was recovered (*Ber.*, 1886, **19**, 2582; *Annalen*, **247**, 85).

This is to quote but one instance out of many in which this mode of procedure led to the desired result in the hands of this investigator in the course of his extended researches on alkaloidal bodies.

In the more recent researches of Emil Fischer on the sugar-group, the same principle is repeatedly made use of. Thus, to take a single example, the synthetical inactive mannonic acid forms, as it were, the centre from which the principal trunk lines of his investigation radiate in the most wonderfully symmetrical manner. This inactive mannonic acid, by conversion into the strychnine salt, can be separated into its active enantiomorphic isomerides, from which by suitable transformations, some of which we shall presently see were the outcome of other work of Pasteur's, was ultimately reached the long-sought goal of optically active sugars identical with those which have from the earliest times been so closely connected with the physiology of the organised world.

It is worthy of notice that this method of racemoid fission has recently been ingeniously improved by Marckwald (*Ber.*, 1896, **29**, 43) in connection with his syntheses of optically active bases. On converting the racemoid base into the acid dextro-tartrate, the salt of one of the components of the racemoid is more insoluble than the

other, and this more insoluble one can be easily purified by crystallisation, but not so the other, which always remains more or less impure. On now, however, converting the original racemoid into the acid *lævo*-tartrate, it is the salt of the other component which is the more insoluble, and so this can then be easily purified by crystallisation. Thus in this way both components of the racemoid are obtained in a state of purity. These relations are rendered more apparent by the following diagram:



Hitherto, the separation of the enantiomorphic isomerides of a racemoid by interaction with an asymmetric or optically active body has only been carried out successfully by combining racemoid acids with active bases, and conversely by combining racemoid bases with active acids. It might, however, be inferred that this method should lend itself to decomposing racemoid acids and racemoid alcohols, by preparing from them ethereal salts with active alcohols and active acids respectively. The attempts to effect a separation by these means have so far failed; thus Simon (*Bull. Soc. Chim.*, 1894, [iii], 11, 760—767) etherified ordinary inactive lactic acid with active amyl alcohol, but obtained no selective etherification, and inasmuch as the product was a liquid there was no separation of the optically isomeric ethereal salts. I have also, in conjunction with Mr. Price, recently prepared the following salts in which such a separation might quite conceivably have taken place:

Amyl (lævo) glycerate (inactive).	Amyl (inactive) glycerate (dextro).
,, diacetylglycerate ,,	,, diacetylglycerate ,,
,, dibenzoylglycerate ,,	,, dibenzoylglycerate ,,

No separation was, however, obtained, and this is the more significant, as in the case of the amyl (lævo) dibenzoylglycerate (inactive) the product is beautifully crystalline (Trans., 1897, 71, 253).

The third and last method of obtaining the resolution of inactive racemoids, and which is in some respects the most remarkable of the three, is also due to Pasteur, and, as in the case of the first, its discovery was due to one of those chance occurrences which are only observed and seized upon by the eye of genius. It had long been

known that impure solutions of calcium tartrate not unfrequently become turbid and enter into fermentation during warm summer weather, and Pasteur noticed one day that a tartrate solution of his had become thus affected; now I think there can be no doubt that most chemists would under the circumstances have poured the liquid down the sink, disgusted that their experiment had thus been spoilt by the presence of this impurity. But an interesting problem at once suggested itself to Pasteur's active mind; how would the two enantiomorphic forms composing the racemate be affected by this agency, the living ferment? This is his own account of what takes place on submitting this question to experimental investigation:

"On placing the ammonium racemate under the same conditions, it enters into fermentation. The same ferment is observed and everything points to matters running the same course as in the case of the dextrotartrate. But if the progress of the operation be followed with the polarimeter, it soon becomes apparent that there is a profound difference between the two experiments. The initially inactive liquid becomes perceptibly lævorotatory, and this rotation gradually increases and attains a maximum. The fermentation is then interrupted. There is now no trace of the dextrotartaric acid left in the liquid, which on being evaporated and treated with an equal volume of alcohol yields a fine crop of crystals of ammonium lævotartrate.

"Two different points in this phenomenon require emphasizing. As in every true fermentation, there is a substance which undergoes chemical alteration, and corresponding with this there is the development of an organism belonging to the fungi. On the other hand, and it is just to this that I would in the present instance draw your attention, the lævo-salt is respected by the ferment which causes the destruction of the dextro-salt, and this in spite of the absolute identity of the physical and chemical properties of both which prevails as long as they are not submitted to asymmetric influences.

"Here we have then that molecular asymmetry which is peculiar to organic matter influencing a physiological process, and influencing it, moreover, by modifying the chemical affinities. There cannot be the slightest doubt that the single and exclusive cause of the difference between this fermentation and that which takes place in the case of the dextrotartaric acid, is the difference in the intramolecular arrangement of the lævotartaric acid.

"Thus the conception of the influence of the molecular asymmetry of natural organic products is introduced into physiological studies, through this important criterion (optical activity), which forms perhaps the only sharply defined boundary which can at the present day be drawn between the chemistry of dead and living nature."* (*Lectures on Asymmetry.*)

* The asymmetric nature of living matter was ever present to Pasteur's mind, and he was always ready to discern applications of this fertile idea. Thus many years later, in 1886, in commenting on a paper by Piutti on the isomeric asparagines read before the Academy, he calls attention to the fact that one asparagine is sweet whilst its optical antipode is insipid, and refers this difference to the different action of these two asymmetric isomers on the asymmetric matters present in the tissue of the gustatory nerve. (*Compt. rend.*, 1886, **103**, 138.)

You will notice that Pasteur on this, as on so many other occasions, does not confine himself to chronicling the simple fact observed, but fitting in, as it does, with a train of thought which has long filled his mind, he does not hesitate to give expression to a general principle and to indicate its far-reaching importance. We shall see presently how the subsequent experience of thirty-seven years has justified the conclusions drawn from what might appear such slender and restricted experimental data.

This third method of racemoid fission discovered by Pasteur has indeed proved not to be an isolated phenomenon confined to the tartaric acids, but an invaluable instrument in experimental science of the widest utility, employed as it has been by numerous investigators in swelling our knowledge of that aristocracy of chemical compounds, which possess, in addition to all the commonplace and vulgar physical attributes, the distinctive seal of *noblesse*—optical activity.

It would be impossible for me here to attempt to place on record even the names of those numerous optically active compounds our acquaintance with which is wholly dependent on this subjection of racemoids to the selective action of micro-organisms, indeed the method seems to be well nigh of universal application in the case of all racemoid bodies which are capable of being attacked by these low forms of vegetable life, and selective decompositions of this kind have been effected both by moulds, by bacteria, and by the saccharomycetes or yeasts.

Some confusion concerning the nature of this process appears, however, to exist even among chemists who write text-books on stereochemistry; thus in one otherwise excellent treatise on this subject is to be found grouped under the same heading, as though closely allied, on the one hand the isolation of various active bodies from their racemoids by the agency of living organisms, and on the other, the production of active bodies by the fermentation of compounds already active. Thus there is no necessary connection whatever, for instance, between the production of lævotartaric acid by the fermentation of racemic acid and that, for example, of lævolactic acid in the fermentation of cane-sugar discovered by Schardinger (*Monatshefte*, 1890, 11, 545). The two processes would obviously only be comparable if it could be shown that the cane-sugar first yielded ordinary inactive lactic acid and that this racemoid was then selectively decomposed or fermented with lævolactic acid as the residue.

Indeed, in most cases, these selective fermentations have been very imperfectly studied, not only are we in general left wholly in the dark as to the nature and purity of the ferment employed, but there is no evidence as to whether the micro-organism only decomposes one

enantiomorphic isomeride more rapidly than the other, or whether it leaves one entirely intact.

Even in the case of Pasteur's original discovery of this remarkable process, he unfortunately gives no description of the organism, although it appears to have been a species of *Penicillium*, but it is difficult to ascertain from his account whether the organism attacked the lævo-tartaric at all or only with more difficulty than the dextro-compound.

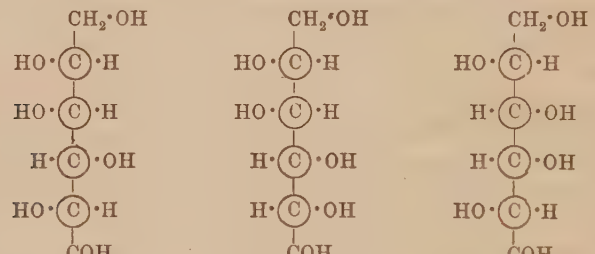
The great value of this method depends on the possibility of applying it to racemoids of such widely different types, if suitable microbes can be found for the purpose. Thus of the three available classes of micro-organisms, the moulds are the most catholic in their tastes, decomposing by way of oxidation suitable solutions of alcohols both mono- and poly-hydric, hydroxy-acids, and carbohydrates; this catholicity of taste, however, renders them less certain as selective agents and leads to their effecting the simultaneous oxidation of both enantiomorphic isomerides; the yeasts, on the other hand, appear to be only available for the decomposition of the aldoses and ketoses, whilst various forms of bacteria have been found to ferment poly-hydric alcohols, hydroxy-acids, and the several types of the carbo-hydrates.

Enantiomorphism being, as Pasteur pointed out, the closest approach to identity which can exist between two molecules, and as this minute difference is quite sufficient for two such molecules to be in many cases quite differently affected by micro-organisms, it is surely not surprising that isomerides which are less closely related than such enantio-morphic ones should also often present wholly different obstacles to microbial decomposition. This has actually been found to take place by those who have systematically studied the action of particular fermenting organisms on fermentable isomerides. A good example of this is furnished by the structurally identical but configuratively different hexahydric alcohols, mannitol and dulcitol,* for which it has been shown that some micro-organisms will ferment mannitol but not dulcitol, whilst others will ferment both isomerides; on the other hand, so far as I am aware, no microbe is known which ferments dulcitol but not mannitol. What is, however, particularly remark-able in connection with these phenomena is that the configurative difference between two such isomerides as mannitol and dulcitol may be of far greater importance as regards their behaviour towards micro-organisms than much more profound changes in molecular structure, thus an organism which ferments mannitol, but not the closely allied dulcitol, may yet be quite capable of attacking the far more remotely related glycerol.

* Percy Frankland and Fox; P. Frankland and Stanley; P. Frankland and Frew, *Proc. Roy. Soc.*, **46**, 345; Trans., 1891, 253; 1892, 254.

More recently, this interesting connection between configuration and fermentability has been investigated with reference to the sugars and their decomposition by yeasts (Emil Fischer and Thierfelder, *Ber.*, 1894, 27, 2031). The results, so far as they are at all comparable with those to which I have just referred, confirm them in a remarkable manner, inasmuch as of the two sugars so closely related to mannitol and dulcitol, namely, *d*-mannose, and *d*-galactose, the *d*-mannose is found to possess a configuration of its molecule which admits of much more ready fermentation by yeasts than does the configuration of the *d*-galactose molecule so closely related to the dulcitol molecule which, as I have pointed out above, is so much more refractory to bacterial decomposition than the mannitol.

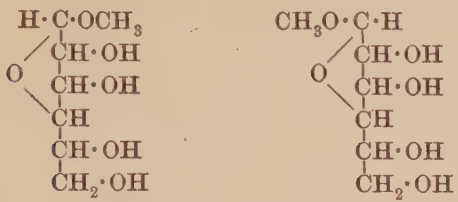
Another interesting and very suggestive result arrived at in these investigations by Emil Fischer and Thierfelder, is, that only those hexoses are fermentable by yeast which have a configuration very closely resembling that of ordinary grape-sugar, thus:



d-Glucose. (Grape-sugar.) *d*-Mannose. *d*-Galactose.

It will be seen that the configuration of *d*-mannose and of *d*-galactose respectively only differ from that of *d*-glucose in the transposition of a single group.

We have already seen that Pasteur clearly indicated, 37 years ago, that this phenomenon of selective fermentation doubtless depended on the dissimilar interaction of asymmetric bodies contained in the living cells, with the asymmetric molecules of the two isomerides, and this explanation of the essential mechanism of the process has recently been strikingly confirmed by the investigations of Emil Fischer (*Ber.*, 1894, 27, 2985, 3479) on the action of enzymes. The action of these enzymes, which are certainly themselves asymmetric, is shown by Fischer to be dependent on the configuration of the compounds which they hydrolyse; thus, to take, perhaps, the simplest example of their selective action on glucosides and polysaccharates:



There are found to be two isomeric methylglucosides, for which the above formulæ have been respectively proposed, and of these the α-methylglucoside is decomposed by invertase, whilst β-methylglucoside remains unaltered.

Thus the phenomenon of the selective decomposition of asymmetric bodies by living organisms is still more clearly attributable to the action of asymmetric reagents, now that similar selective phenomena exhibited by the soluble ferments or enzymes is found also to be regulated by the asymmetry of the compounds on which they act.

A few weeks ago, E. Buchner (*Ber.*, 1897, **30**, 117) announced that a soluble principle* giving rise to the alcoholic fermentation of sugar, may be extracted from yeast, and for which the name *zymase* is proposed; should this highly interesting observation prove to be correct, and there appears to be no reason to doubt its accuracy, the phenomena of fermentation will obviously be brought still more closely and unmistakably into line with those attending the chemical interaction of asymmetric molecules.

Transformation of Tartaric Acids.

The three methods of racemoid resolution discovered by Pasteur have thus, not only constituted almost the exclusive machinery by means of which the list of optically active compounds have been extended, but they have been the means of disclosing one of the most important types of chemical reaction, namely, that in which two asymmetric compounds enter into reaction with each other. But there were other remarkable changes which Pasteur discovered in connection with the tartaric acid molecule, and in the due appreciation of which he was 30 years in advance of the time. These discoveries, after remaining almost unheeded for a generation, have quite recently proved of extraordinary fertility, and their skilful application has led to some of the most important developments.

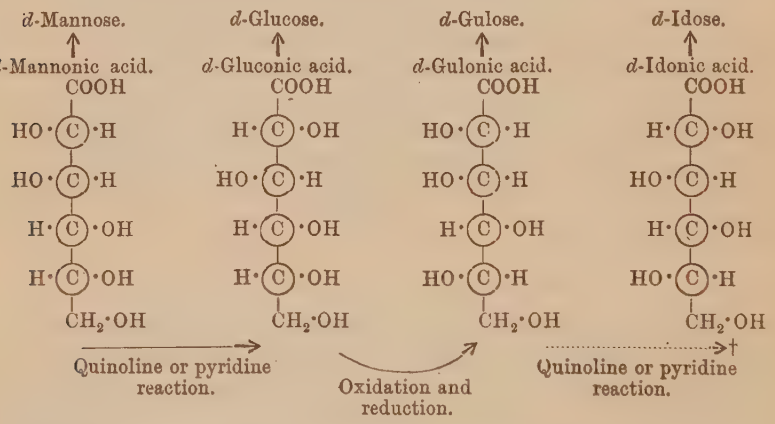
Already in 1853 (*Annalen*, **88**, 212), Pasteur found that ordinary dextrotartaric acid, on being heated with water, or in the form of its

* It is worth mentioning in this connection that Schunck had obtained true alcoholic fermentation by means of *erythrozyme*, a substance present in extract of madder and precipitable from the latter by dilute hydrochloric acid. See Liebig, *Ann. Chim. Phys.*, 1871, [iv], **23**, 35.

cinchonine salt, underwent a partial change, and that after being subjected to this treatment, there were present, in addition to unaltered *d*-tartaric acid, some racemic acid and a new form of tartaric acid, which resembled racemic acid in being inactive to polarised light, but differed from racemic acid in not being decomposable into left and right-handed tartaric acids. Thus this simple mode of procedure accomplishes the double feat of transforming dextrotartaric acid into lævotartaric acid, and of producing a fourth kind of tartaric acid, which, whilst inactive, is yet quite distinct from racemic acid, inasmuch as it does not admit of resolution into enantiomorphic isomerides.

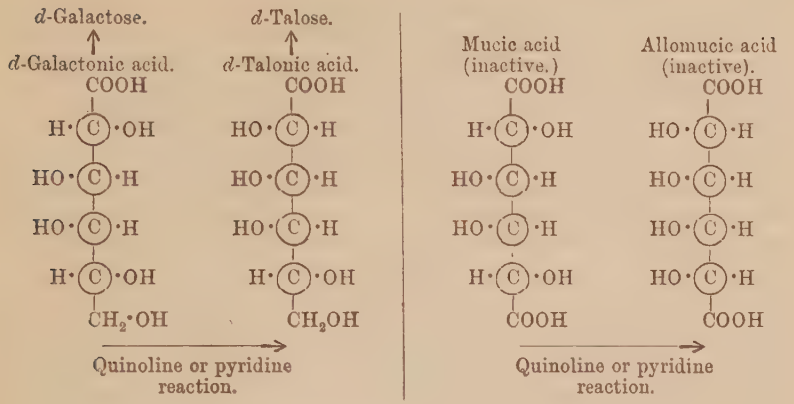
It is this mode of transformation which has been applied with such brilliant results by Emil Fischer, in whose hands this artifice has proved invaluable in the exploration of the sugar-group.

A glance at the following table will convey the best idea of the *rôle* which this method of transformation, discovered by Pasteur, has played in the researches of Emil Fischer.* (*Ber.*, 1894, 27, 3189—3232).



* In this diagram the transformations indicated as "quinoline or pyridine reactions" are precisely similar in their nature to that discovered by Pasteur in the case of tartaric acid, consisting as they do of a rearrangement of the H and HO groups attached to the asymmetric carbon atom which is attached to the COOH group in each case.

† This transformation has not actually been carried out for the *d*-acid, but the corresponding one for the *l*-acid has been effected.



Researches on Malic Acid and its Derivatives.

The tartaric acids and their derivatives were, however, not the only optically active compounds to which Pasteur directed his attention, for as early as 1852 (*Annalen*, **82**, 331; *Ann. Chim. Phys.* [iii], **38**, 441, and **49**, 8) malic acid and its compounds, together with aspartic acid (*Ann. Chim. Phys.*, [iii], **34**, 30), were also brought within the scope of his investigations.

A short excursion into these researches on malic acid is particularly instructive, for whilst in the case of the tartrates not only the facts but also the explanations given by Pasteur have, broadly speaking, stood the test of time, in the case of the malates his theoretical conceptions were, in part, soon shown to be in conflict with the truth.

Throughout Pasteur's investigations on optically active compounds, he was possessed with the idea that the molecular dissymmetry which is betrayed in this optical effect could only be produced by vital agency, in fact he was never tired of insisting on the indissoluble connection between asymmetry and life. The weighty considerations which had led him into and strengthened him in this conviction are apparent from the following words of his own:

"Take any asymmetric body you like, and you may be sure that its asymmetry will disappear as soon as you expose it to only moderately energetic chemical reactions. Thus tartaric acid is asymmetric. Pyrotartaric acid * is not; malic acid is asymmetric whilst maleic and fumaric acids discovered by Pelouze are not. Gum is asymmetric, mucic acid is not.

"Thus the artificial bodies are devoid of molecular asymmetry, and I know of no profounder difference than this between ordinary bodies and those which are produced under the influence of life." (*Lectures on Asymmetry.*)

* Ordinary pyrotartaric acid, $CH_3 \cdot C H(COOH) \cdot CH_2 \cdot COOH$, is now known to be a racemoid and has recently been resolved by Ladenburg (*Ber*, 1895, **28** 1170) by crystallisation of the strychnine salt.

These views received a rude shock when, soon after 1850, Dessaignes announced that he had obtained aspartic acid by heating the ammonium salts of fumaric and maleic acids. This statement was as incompatible with Pasteur's theories as was the memorable announcement of Mitscherlich concerning the identity of the sodium ammonium salt of racemic and tartaric acids, for if M. Dessaignes' facts were correct they would mean that he had accomplished what Pasteur firmly believed to be unrealisable, the preparation by chemical means of an optically active molecule from an inactive one. Of such pressing importance did the settlement of this doubt appear to Pasteur, that, with his usual restless energy, he at once hastened from Strassburg to Vendôme and obtained from Dessaignes a specimen of his artificial aspartic acid, which he had no difficulty in showing was not really identical with the natural aspartic acid, but only an inactive isomeride. This inactive aspartic acid he also converted by the well-known method of Piria into malic acid, and this malic acid he found, in accordance with his anticipations, differed from the natural one in being inactive to polarised light. The comparative study of the active and inactive malates he found a far more perplexing task than had been the similar investigation of the tartrates, for whilst in some cases the hemihedrism of the active malates was sufficiently apparent, in others it was much obscured or even entirely absent, the forms being sometimes absolutely identical with those of the inactive compounds.* Notwithstanding, Pasteur remained inflexible as to the relationship between the two malic acids, placing his whole confidence in optical activity being the outward and visible sign of the inward, molecular asymmetry, and dismissing the appearance of hemihedrism in crystalline form as a criterion of altogether secondary importance. Thus his mental attitude is most concisely revealed by the following extract :—

"Who could, after this, be in any doubt concerning the relationship between the molecular arrangements present in these two salts (the calcium salts of active and inactive malic acids)? Is it not perfectly clear that in the case of the inactive malic acid we have an acid identical with the natural malic acid, but with a suppression of the molecular asymmetry?

"It is the untwisted natural malic acid, if I may so express myself. If the atomic arrangement of the natural acid be represented by a spiral staircase, then the artificial malic acid is the same staircase with the same steps, but straight instead of spirally disposed.

"It might be asked whether the new malic acid is not the para-acid of this series, that is, the compound of the dextro- and lævo-malic acid. But of that

* The presence of hemihedrism is now ascertained by means of "etching-figures," and, according to H. Traube, *all* the crystals of optically active substances which have been thus examined by etching exhibit hemihedrism, and all apparent departures from Pasteur's original principle have, so far, disappeared on being submitted to this test. (*Ber.*, 1897, **30**, 288.)

there is only very little probability, for in that case not only would *one* active body have been made from an inactive one, but there would have been *two* such prepared, one dextro- and the other lævo-rotatory.

"Moreover, I have similarly found that just as there is a non-asymmetric inactive malic acid, so there is a non-asymmetric inactive tartaric acid, which is very different from racemic acid, and which cannot be resolved into a dextro- and a lævo-rotatory tartaric acid. There can no longer be any doubt that this is a dextro- or a lævo-rotatory tartaric acid which has become non-asymmetric.

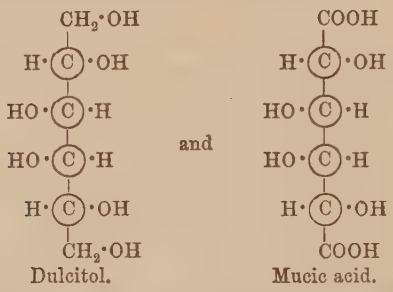
"Similarly, I have discovered the inactive amyl alcohol, from which a whole series of inactive products can be derived which correspond to the series derivable from the active amyl alcohol.

"Thus, thanks to the discovery of these inactive bodies, we are in possession of a fruitful idea; a substance is asymmetric, dextro- or lævo-rotatory, but by certain processes of isomeric metamorphosis, which must be sought and discovered for each particular case, the substance can lose its molecular asymmetry, it can untwist itself, to use a gross simile, and can arrange its atoms in such a fashion that it becomes superposable with its mirror-image. In this manner every asymmetric body affords four variations, or better four distinct subdivisions; the dextrorotatory body, the lævorotatory body, the compound of the dextro- and the lævo-rotatory bodies, and the body which is neither dextro- nor lævo-rotatory, nor formed by the union of these two." (*Lectures on Asymmetry.*)

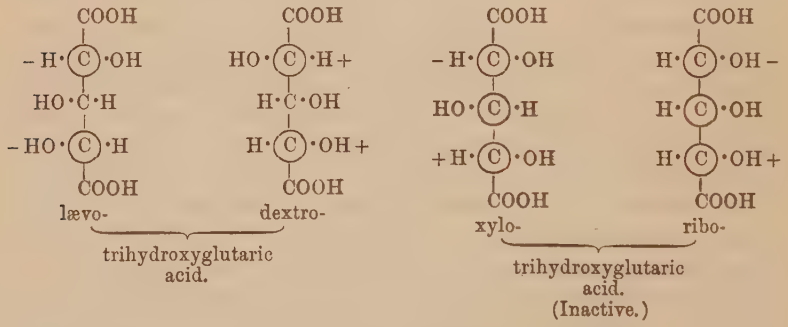
At the present day, it is, of course, easy to detect the errors committed by Pasteur in the above discussion, and it is particularly instructive to notice how he was only deterred from grasping the truth in its entirety through too obstinate adherence to a single preconceived idea. Thus, had Pasteur only kept his mind open to the possibility of building up an asymmetric molecule artificially, he would have naturally recognised the inactive malic acid in its true character, namely, as the analogue of racemic acid, instead of inventing a new class of bodies for its reception. This new class of bodies, which was entirely the creation of Pasteur's imagination, included substances isomeric with asymmetric bodies but in which the asymmetry was abolished by a rearrangement of the atoms, and this class of bodies, which he had imagined to erroneously meet the case of inactive malic acid, he subsequently discovered the real existence of when he actually obtained truly inactive or mesotartaric acid. Pasteur had thus, in the very act of putting this wrong interpretation on inactive malic acid, made a most important addition to the theory of asymmetric compounds by postulating the existence of this fourth type of isomer for asymmetric compounds, namely, that in which the compound is neither dextro- nor lævo-rotatory nor yet formed by the union of these. This theoretical conception he subsequently, as we have seen, placed upon a sound experimental basis by the actual discovery of mesotartaric acid. I need hardly remind you that this fourth type does not exist for every asymmetric compound, as was erroneously supposed by

Pasteur, but only for those which, like tartaric acid, the tetra- and hexa-hydric alcohols, and the hydroxy-dibasic acids, can, by a suitable stereometric arrangement of the groups, have their molecules divided into two symmetrical halves, the optical effect of the one-half neutralising the optical effect of the other within the molecule.

Thus we have easily intelligible instances of true inactivity in



whilst especially interesting in this connection are the four stereoisomeric trihydroxyglutaric acids, two of which are active and two truly inactive:



Before leaving the subject of malic acid, it is worthy of note that it is in connection with this acid that undoubtedly one of the most important discoveries relating to optically active bodies has been made since the time of Pasteur; I refer to the remarkable transformation of lævomalic acid into dextromalic acid, and *vice versâ*, through the medium of the corresponding chlorosuccinic acids which has been accomplished by Walden (*Ber.*, 1896, **29**, 133).

L-malic acid → *d*-chlorosuccinic acid → *d*-malic acid
„ „ ← *l*-chlorosuccinic acid ← „ „

The dogma that asymmetric bodies cannot be artificially prepared, led Pasteur into some abstruse speculations concerning their production in nature, which have hitherto only received negative illumination

from direct experiment. He points out that it is necessary, and quite sufficient, to suppose that at the genesis of a vegetable organism some asymmetric force must be in operation, and suggests that light, electricity, magnetism, and heat may be subject to asymmetric influences of a cosmic nature. Are these, he asks, perhaps connected with the motion of the earth, or with those electric currents by means of which physicists explain the magnetic poles of the earth? At any rate either asymmetric forces are wanting in our synthetical reactions, or they are without influence on the latter, possibly in consequence of the rapid course of such chemical changes.

Nor did Pasteur simply propound these questions, but, on the contrary, the great master of the experimental method undertook a bold campaign into this highly speculative domain, from which, however, he soon deemed it more prudent to retreat, doubtless realising that his intellectual forces might be more advantageously employed in other directions than in a territory where only negative victories were to be won. Thus at Strasburg he actually had powerful magnets constructed with a view to introduce dissymmetric influences during the formation of crystals. At Lille, again, in 1854, he had a clockwork arrangement made with which he intended, by means of a heliostat and reflector, to reverse the natural movement of the solar rays striking a plant, from its origin to its death, so as to see whether in such an artificial world, in which the sun rose in the west and set in the east, the optically active bodies would not appear in forms enantiomorphic with those which the existing order of nature provides. Pasteur, however, soon realised, doubtless instructed by his experience gained in other voyages of discovery on which he had already embarked, that the task of turning the Creator's universe upside down was even beyond his experimental skill, recognising that, however he might reverse these external influences, he would still have to deal with the asymmetric agencies already present with all their irresistible, albeit latent, power, in the germ of life itself, and that, without the possibility of spontaneous generation, there was also no possibility of realising this dream of a new living world with its plants and animals producing the optical antipodes of the natural celluloses, albumens, starches, sugars, terpenes, &c., for the edification of the stereochemical philosopher.

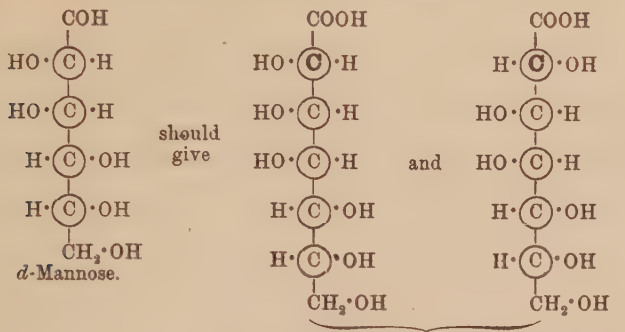
Similar abortive attempts have been more recently made by other investigators. Thus, Boyd (Dissertation, Heidelberg, 1896) prepared stilbene bromide in a powerful magnetic field, but only obtained the ordinary compound. Again, he found that the mandelic acid obtained by the reduction of benzoylformic acid in a magnetic field was inactive, nor was an active mandelic acid obtained either by effecting this reduction in the presence of dextrotartaric acid, or of lævomandelic acid.

The dogma of the impossibility of producing asymmetric compounds by our existing synthetical methods was, however, discredited within a few months after its enunciation by Pasteur in the terms which I have just quoted, for in 1860 a discovery of far-reaching importance was made in this country by two investigators, of whom one unfortunately lives only in the annals of our science, and in the memory of those who had the privilege of knowing his singularly attractive personality, whilst the other is still in the front rank of our society militant, his zeal for research being of that rare order which is unimpaired even by a long series of successes achieved over a period of more than a generation. It was in 1860 that Perkin and Duppa prepared from succinic acid a tartaric acid which Pasteur himself identified as racemic acid, so, to use the words employed by Pasteur before, the synthesis had thus been accomplished not only of one, but actually of two asymmetric molecules.

Had Pasteur only slightly modified the terms of enunciation of the dogma, it might indeed stand unchallenged still, for the feat even now remains unaccomplished, saving by the agency of life alone, of building up from symmetric materials a single asymmetric molecule, without at the same time building up an equal number of asymmetric molecules enantiomorphic with the first, that is, the direct synthesis of an optically active compound is still a dream of the future. Indeed, the relationship between optical activity and life is closer than was probably suspected even by Pasteur, and optically active compounds may actually be compared with living organisms, for just as when we have once got life there is nothing more easy than to convert inanimate into living material, indeed the great difficulty of modern times is to check the prodigality of such conversion, so if we have once got an active compound we can not only attach inactive matter to it rendering the new substance active as a whole, but the part added may itself become active, and the qualitative activity of the added part will depend on the qualitative activity of the body which has activated it, just as the nature of the offspring is conditioned by the nature of the parent. The doctrine of heredity is in fact applicable with absolute rigidity to the reproduction of asymmetry. This will be evident from a concrete example.

Thus mannose by means of the cyanhydrin reaction can be converted into mannoheptonic acid, in which a new asymmetric carbon atom has been created, and around which, therefore, the four different groups can be arranged in two different ways, so as to give rise to two isomeric acids. Each of these, it might be supposed, would have an equal chance of formation by artificial synthesis, but, as a matter of fact, as Emil Fischer has shown, one of these is *exclusively* formed; the new active

it by the asymmetry of its parent (E. Fischer, *Ber.*, 1894, **27**, 3210; 1889, **22**, 370; Hartmann, *Annalen*, 1892, **272**, 190).



Two *d*-mannoheptonic acids, of which one is exclusively formed.—[N.B. The newly created asymmetric carbon atom is represented in black-faced type.]

In making the above remarks as to the hitherto unaccomplished achievement of building up an optically active substance without the agency of life, I must, in passing, refer to the startling announcement recently issued by Dr. John Pickering (*Proc. Roy. Soc.*, 1896, **60**, 337) that he has succeeded in synthesising from inactive materials certain proteid-like substances possessing a high rotatory power. These compounds are obtained by heating together such substances as metamidobenzoic acid, biuret, and phosphorus pentoxide; again, metamidobenzoic acid, alloxan, and phosphorus pentoxide; and again, paramidobenzoic acid and phosphorus pentachloride. Now, although numerous experiments of a physiological character have been made with these products, the author is apparently wholly oblivious of the fact, assuming his observations to be correct, that he has made a chemico-physical discovery of the first order. Dr. Armstrong has been kind enough to give prominence in the columns of *Nature* to the epoch-making nature of this discovery, and to ask for further particulars, but the author is apparently so absorbed with the importance of the physiological side of his observations that he has not yet found time to take any notice of the interest which his researches have excited in the chemical world.

This is, in outline, the work of Pasteur in the domain of pure chemistry and molecular physics; as an example of the combination of rare experimental skill and precision with consummate deductive power, it stands out, I think, as one of the most remarkable and artistic monuments in the annals of our science. This work, begun, continued, and ended within the period extending from 1844 to 1860, is an achievement on which an investigator might look back with pride at the close of a lifetime, and yet, on its completion, Pasteur stood only on the threshold of

his great career. It has been my endeavour to show how Pasteur's work in this special field forms, not only the foundation, but nearly the whole of the framework on which that great structure of stereochemistry has been subsequently raised. The point at which he left this investigation of the phenomena of asymmetry was almost the ultimate limit to which this study could at that time be profitably carried, and for further progress it was necessary that those gigantic labours in revealing the structure and constitution of chemical molecules, which were the dominant feature of the development of our science during the greater part of the past thirty years, should be carried out. It was only after such knowledge of chemical constitution had been gained that that progress in stereochemistry which is associated with such names as Wislicenus, Le Bel, Van't Hoff, Baeyer, Emil Fischer, and many others, could take place. But great as that progress has been, it only serves to emphasize the more the extraordinary completeness of Pasteur's preliminary exploration of the field. To quote the words recently pronounced by Emil Fischer, "If we look back to-day on this wide domain, we are forced to admit that, notwithstanding the large number of new observations, and notwithstanding all the advances in detail that have been made, there is hardly a new fact of fundamental importance which has been added to his discoveries."

Pasteur's chemical work was commenced, as we have seen, when he was assistant to M. Balard at the École normale in Paris, but already, in 1848, he was appointed Professor of Physics, at the age of 26, at the Lycée at Dijon, and three months later he was called to act as Deputy-Professor of Chemistry at the University of Strasburg, succeeding to the chair there in 1852. It was here that he met his future wife, the daughter of M. Laurent, Rector of the Strasburg Academy; they were married in 1850, and it is related how Pasteur was so engrossed in his laboratory that he entirely forgot the wedding-day and had to be fetched for the ceremony by one of his friends. The marriage was, however, an unusually fortunate and happy one, as will be evident from the following description given by one who had the privilege of being for years the collaborateur (Roux, *Agenda du Chimiste*, Paris, 1896) of the great master.

"The career of Pasteur cannot be properly understood without a knowledge of his family and above all of Mme. Pasteur. From the first days of their united life, Mme. Pasteur realised what manner of man she had married, and endeavoured to protect him from the difficulties of life, taking upon herself the cares of the house, so that he might keep his mind perfectly free for his researches. Mme. Pasteur loved her husband to the extent of understanding his labours. In the evening she wrote to his dictation, asking for explanations, for she took a living interest in the hemihedral facets and in the attenuated viruses. Moreover, she saw well that ideas become clearer through exposition, and that nothing is more conducive to the suggestion of new experiments than

the description of those which one has just carried out. Indeed, Mme. Pasteur was not only a perfect companion to Pasteur, she was his best assistant."

Studies on Fermentation.

A new chapter in Pasteur's life opens with the year 1854, when, at the age of 32, he was nominated the first Dean of the Faculty of Sciences which had just been created at Lille. In this capacity he at once realised that the work of his department should, to some extent, be brought into touch with one of the leading industries of the district—the manufacture of alcohol from beetroot and grain—and he accordingly offered courses of lectures on fermentation, and with his characteristic energy threw himself into the serious study of this subject.

I will not trespass on your time by passing even in the briefest review the history of the progress made in the knowledge of fermentations before the subject was attacked by Pasteur; suffice it to say that at this time fermentation processes were not generally regarded as vital phenomena at all, for the dominant opinion concerning them was that of Liebig, who viewed the classical transformation of sugar into alcohol as a purely chemical process depending, not on the living yeast cells which the microscope had revealed, but on the dead yeast undergoing *post-mortem* decomposition:

"Beer yeast, and, in general, all animal, and vegetable matters in putrefaction, impart to other bodies the state of decomposition in which they are themselves. The movement, which by the disturbed equilibrium is impressed on their own elements, is communicated also to the elements of bodies in contact with them."

Pasteur had been indirectly brought in contact with fermentation phenomena in the course of his researches on asymmetry, for amongst the optically active compounds known at the time, was the amyl alcohol which is obtained as a by-product in a number of fermentations. In his examinations of this compound and its derivatives (*Compt. rend.*, 41, 296; *Annalen*, 1855, 96, 255), he found, it may incidentally be remarked, that none of the crystallisable substances exhibited hemihedral faces. The manner in which the study of this amyl alcohol launched Pasteur into the investigation of fermentation phenomena with a preconceived idea opposed to Liebig's doctrine, is clearly set forth in his own writings. Liebig's theory would obviously interpret the optical activity exhibited by amyl alcohol as conditioned by the asymmetry of the sugar from which it is derived in the fermentation process, but Pasteur distinctly states that he considers the molecule of amyl alcohol to be too remotely related to that of sugar to have preserved the dissymmetry of the latter. The dissymmetry of the amyl alcohol must, therefore, be a new creation, so to speak, and such creation of an asym-

metric molecule was, in Pasteur's opinion, as we have seen, only possible by the intervention of life. It would follow, then, almost as a necessary corollary, that the fermentation in which the amyl alcohol had been formed must be a vital process, and not the purely chemical transformation which Liebig would have us believe it to be. We have seen what a tremendous power a preconceived idea, even though a partially erroneous one, proved in the hands of Pasteur in the case of his investigations on molecular dissymmetry, we must now follow the consequences which resulted from such a preconceived idea in the domain of fermentations.

In 1857, Pasteur (*Ann. Chim. Phys.*, [iii], 52, 404) brought before the scientific world the results of his researches on the lactic fermentation, the first of that series of masterly investigations which he was to pursue during the next 20 years. In 1860, this was followed by a paper (*Ann. Chim. Phys.*, [iii], 58, 323) on the alcoholic fermentation.

In the lactic fermentation, Pasteur noticed that a greyish, solid material was deposited, and that the quantity of this increased during the process; on examining some of this substance under the microscope, he found that it consisted of very minute corpuscles, rod-like in shape and quite distinct from the yeast cells observed in the alcoholic fermentation. He took a trace of this grey material and introduced it into an artificial solution of sugar, to which he had added some decoction of yeast and chalk, and soon had the intense satisfaction of witnessing the lactic fermentation in full activity in this liquid. From this fermenting liquid he transferred again a minute trace into another similar solution of sugar and so on, invariably obtaining the same fermentation, invariably finding, also, the same corpuscles in the deposit.

Pasteur, however, at once realised that Liebig and his supporters might attribute the fermentative change in the sugar to the decomposition of the albuminoids present in the decoction of yeast employed in his experiments, and he therefore determined to cut off this retreat, which through its inaccessibility had so long sheltered Liebig's theory, which, destitute as it was of any sound foundation, could not have survived, even for a day, if exposed to the direct fire of experimental criticism. To this end, Pasteur entirely abolished the albuminoids in his fermentations, replacing them by ammonium salts, and in these solutions of pure sugar, with nothing but mineral additions, he demonstrated that the yeast grew and multiplied, and that its growth was accompanied by the conversion of the sugar into alcohol and carbonic anhydride, whilst, similarly, those totally distinct living corpuscles, to which he gave the name of *levure lactique*, proliferated in solutions of the same composition, and their multiplication was accompanied by the transformation of the sugar into lactic acid:

"As for the interpretation of the group of new facts which I have met with in the course of these researches, I am confident that whoever shall judge them with impartiality will recognise that the alcoholic fermentation is an act correlated to the life and to the organisation of these corpuscles and not to their death or their putrefaction, any more than it will appear as a case of contact action in which the transformation of the sugar is accomplished in the presence of the ferment without giving or taking anything from it."

It is the firm conviction in Pasteur's mind of the dependence of the fermentative process on the life of the organism, and his repugnance to the shallow form of words dignified by the name of theory, and which simply served to cloak the chemical ignorance of the time concerning these mysterious phenomena of fermentation, that obviously acted as the stimulus in these extraordinarily comprehensive and laborious researches, for both his memoirs end with the same words quoted above, as though he enjoyed hearing the sound of the hammer on the last nail knocked into the coffin of the dogma which had by so many years delayed the scientific prosecution of the study of fermentations on the vitalistic lines inaugurated by Cagniard Latour and Schwann.

The amount of new experimental material collected by Pasteur in support of this thesis fills the reader with admiration, whilst his extraordinary power of seeing what others had failed to observe before him, is again exemplified in his discovery of succinic acid* and glycerol as invariable products of the alcoholic fermentation of sugar.

During the progress of these fermentation researches, an important event had occurred in Pasteur's life, for the year 1857 witnessed his removal from the provincial Lille to the metropolis of France, in the palmiest days of the Second Empire. His advancement to the post of director of scientific studies at the École normale in Paris was, however, not an unmixed advantage to Pasteur, as it deprived him of that which he most valued—a scientific laboratory. Nor did there seem to be any prospect of obtaining one, as the French Government of forty years ago appears to have been on much the same level of enlightenment as our own rulers of both parties to-day, in fact one of the ministers publicly informed Pasteur that the Budget could not provide him with the sum of 1500 francs (£60) a year for experimental researches. Looking back upon the political events of the past forty years, it may safely be asserted, I think, that had that ministry and its successors up to 1870 devoted more of their annual Budget to such and similarly solid enterprises, and less to the hollow and wasteful display of a sham militarism, the France of to-day might have been still in possession of the fair provinces it cost her such a pang to surrender.

* It is true that Schmidt had found succinic acid in all fermented liquids already in 1848. See Liebig, *Ann. Chim. Phys.*, 1871, [iv], **23**, 35.

The experimental zeal of Pasteur was not, however, of that order which can be strangled by red tape, and the laboratory which the nameless and long-since-forgotten minister would not concede was constructed at Pasteur's private expense in a garret of the École normale.

In the course of the studies on fermentation which now followed, Pasteur made a discovery which, in respect of its wide and fundamental significance in relation to the economy of nature, is perhaps without an equal amongst his numerous and great achievements. Moreover, the manner in which this discovery was made affords another illustration of his penetrating scrutiny of the smallest detail in the phenomena which passed before him. It was in studying the butyric fermentation that he took, as was his wont, a drop of the fermenting liquid, and examined it in the thin film obtained by mounting on slip and cover-glass under the microscope; but on this occasion he was struck by the fact that, along the periphery of the drop, wherever it was in contact with the air, the bacilli appeared motionless and inert, whilst the bacilli in the central portion of the drop were executing those remarkable movements which form one of the most fascinating spectacles which the microscope provides. The question at once arose in Pasteur's mind, were these vibrios in the centre fleeing from the oxygen at the periphery, and had the latter paralysed the activity of those which had been brought in contact with it? There was nothing more easy than to interrogate them on the subject, by passing a stream of air through a flask containing a liquid in butyric fermentation; nor had he long to wait for the answer, for the fermentation soon slackened and was ultimately arrested. (*Compt. rend.*, 1861, **52**, 346).

Thus was science enriched by the revelation that there exist living forms which grow, multiply, and develop mechanical energy in the absence of that oxygen which it had hitherto been regarded as one of the most far-reaching discoveries to have shown was indispensable for the whole living creation. Moreover, this remarkable life was actually shown to be either destroyed or paralysed by the very element on the presence of which all life was supposed to depend.

We have seen already that Pasteur's first announcement of the resolution of racemic acid into the enantiomorphic tartaric acids was received with incredulity, and it is not surprising that such a revolutionary discovery as this of *anaërobic life*, as he called it, should have raised a perfect storm of opposition. But Pasteur's confidence in his own results was not to be shaken by the kind of criticism which is based on reverence for tradition, nomenclature, and classification, and his firm and uncompromising attitude towards his opponents is well exemplified by the following words of his own:—"Whether the progress of science makes of this vibrio a plant or an animal, it matters little:

but it is a living being, endowed with movement, which lives without air and is a ferment." (*Compt. rend.*, 1861, **52**, 1261.)

This anaërobic life of the butyric ferment was not allowed to remain an isolated observation without bearing on other facts, but, on the contrary, its relationship to other known facts was at once discerned by Pasteur, who already in the same year, 1861, makes another communication to the Academy of Sciences in which he develops in outline that celebrated theory of fermentation which has served to stimulate so many valuable researches. The considerations which led to the evolution of this theory in Pasteur's mind are apparent from the following passage with which he concludes this note:

"Thus beside all the beings known until to-day, and which without exception (as is believed) cannot breathe and nourish themselves but by the assimilation of free oxygen gas, there would be a class of beings possessing such vigorous respiratory power, that they are able to live without the influence of the air by taking oxygen from certain compounds, thus occasioning in the latter a slow and progressive decomposition. This second class of organised beings would be constituted by the ferments, similar in every respect to the beings of the first class, living even as they are, assimilating after their fashion carbon, nitrogen, and phosphates, and also standing like them in need of oxygen, but differing from them, inasmuch as they can, in the absence of free oxygen gas, take this element from compounds of little stability." (*Compt. rend.*, 1861, **52**, 1264.)

Pasteur in his investigation of fermentative phenomena had thus by the year 1861, shown, firstly, the worthlessness of the form of words by means of which Liebig and the chemists of the time sought to banish all biological considerations from the study of these questions. Secondly, he had worked out a method of scientifically attacking these problems, in which, for the first time, both the chemical and biological aspects of the subject received their due share of attention. It is here that we are again brought in contact with those peculiar endowments which were the key to Pasteur's success throughout his career. Just as his brilliant achievements in the domain of asymmetry were due to the facility which he displayed in bridging the gulf between pure physics and chemistry, and co-ordinating the facts belonging to each, so here again we find him closing the breach between chemistry and biology and moving with equal facility along the main lines of each of these sciences, which lines, to continue the simile, differ so much in gauge and gradient that the rolling-stock most suitable for progress on the one is in general wholly useless on the other; but the vehicles of Pasteur's mind were especially remarkable for the adjustability of their gear and gauge, and it is to this altogether exceptional versatility that we owe his successful exploration of the borderlands, which can only be traversed by those capable of adapting themselves to the particular

means of locomotion available in two countries of widely different configuration.

Thirdly and finally, by the systematic use of this new method of investigating fermentation phenomena, he had discovered the possibility of life without air and had collected sufficient experimental data to venture on the new theory of fermentation which he enunciated in the words I have quoted..

The further researches which this new theory stimulated were deferred for some years in consequence of his attention being directed to certain phenomena closely related to fermentation and, indeed, demanding a full and final explanation before satisfactory progress could be made in, to use his own words, "*ces travaux dont la difficulté ne me laisse ni trève ni repos*" (*Ann. Chim. Phys.*, [iii], 61, 488).

Researches on Spontaneous Generation.

The investigation to which Pasteur in the next instance devoted his commanding energies might appear to us at the present time almost a work of supererogation, for, during more than twenty years past, we have heard nothing of that great question which has exercised the mind of man from the earliest ages—Can life originate spontaneously?

Expressions of opinion on this subject are to be found in the writings of some of the greatest authorities of ancient and modern times. Aristotle categorically affirms that "every dry body becoming moist, and every moist body becoming dry engenders animals." Virgil asserts that bees originate within the putrefying carcase of a young bull:

> "Aspiciunt liquefacta boum per viscera toto
> Stridere apes utero, et ruptis effervere costis."

Van Helmont actually supplies the prescription for producing by spontaneous generation the domestic mouse. His formula consists in squeezing some soiled linen into the mouth of a vessel containing some grains of wheat, which arrangement gives rise to the transmutation of the wheat into mice in the course of about twenty-one days. The mice so generated are said to make their appearance in the adult state, both sexes being duly represented.

The interrogation of nature by direct experiment in regard to this problem does not commence until the middle of the last century, when in 1745 Father Needham, an Irish priest, declares in favour of spontaneous generation, convinced by the result of experiments which he had made on quite modern lines, namely, of placing putrescible substances in vessels which he subsequently hermetically sealed and submitted to heat. He assumed that the heat would destroy all life in these materials, and when he afterwards found that an abundance of microscopic living forms made their appearance in these vessels, he

concluded that they had arisen by spontaneous generation. That this investigation carried conviction at the time is shown by the fact that within two years of its publication he was elected a Fellow of the Royal Society, and a little later he had the honour of becoming one of the eight Associates of the Academy of Sciences. It was not until 1763 that these results were challenged by the Abbé Spallanzani in a dissertation which led to a lively dispute between these two divines. By heating the hermetically sealed vessels more thoroughly, and for a longer period of time, Spallanzani obtained results directly opposed to those of the Irish priest ; to these, however, Father Needham raised the objection that the additional torture, to use his own expression, to which Spallanzani had subjected the materials, had enfeebled or perhaps totally destroyed the "vegetative force" of the substances and "entirely corrupted" the air present in the vessels. Needham's objection was subsequently strengthened by the discovery, made by Gay Lussac, that the air present in the hermetically sealed vessels containing various vegetable and animal substances preserved by Appert's process was entirely destitute of oxygen.

This objection was, however, dispelled by Schwann, who in 1837 modified the method of experiment in a most noteworthy manner, namely, by allowing air to enter the vessel containing the putrescible substance which had been sterilised by heat, making this air, however, pass through a tube which was heated nearly to the boiling-point of mercury in a bath of fusible metal. Under these conditions, in nearly all cases again the putrescible or fermentable substances remained intact, but a few experiments gave a contrary result, and the investigation thus failed to convince even its author. Similarly indecisive results were obtained by Ure, Helmholtz, Schultze, who passed the air through chemicals (caustic potash and sulphuric acid), and by Schroeder and Dusch, who in 1854-59 altered the modus operandi again by filtering the air through cotton wool.

This unsatisfactory state of affairs was brought to a crisis when in 1859 M. Pouchet appeared before the Academy with a paper in which he claimed to have proved the possibility of spontaneous generation by admitting artificial air to the sterilised putrescible matters with the result that organised forms of life made their appearance.

To put an end to this confusion twice confounded, the Academy in 1860 gave as a subject for a prize-competition :

"Essayer, par des expériences bien faites, de jeter un jour nouveau sur la question des générations spontanées."

It is at this moment that Pasteur enters the lists, and the circumstance that we have for more than 20 years heard nothing of the doctrine of spontaneous generation is due to the effectual manner in which he successively hurled into the dust the several champions

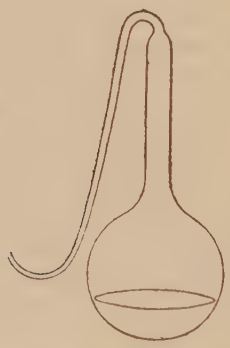
who appeared on its behalf in the intellectual tournament which followed.

Pasteur repeated the experiments of Schroeder and Dusch, but instead of using ordinary cotton-wool he employed gun-cotton (collodion cotton) as the filtering material for the air, and by subsequently dissolving this in a mixture of alcohol and ether, he showed that it had arrested a multitude of living organisms.

Pasteur was also confronted by the difficulty which had so much perplexed his predecessors, namely, that milk developed microscopic growths even after being subjected to boiling for some minutes, but instead of recognising in this any support to the theory of spontaneous generation, he inferred that the milk doubtless contained originally some peculiarly refractory organisms, and by raising the temperature of sterilisation to 110° he found in point of fact that no growths did subsequently make their appearance.

One of the most elegant experimental proofs furnished by Pasteur that air, provided it is deprived of its suspended organisms, is incapable

Fig. 1.



of stimulating into life sterilised organic materials, consisted in placing the organic infusion in a flask, the neck of which was subsequently drawn out into a long tube curved downwards and then upwards, as in the figure, and the extremity of which was left open. On sterilising this, by boiling and then allowing it to cool, the air would obviously enter by this open tube, but the putrescible infusion remained unaltered; and that the germs suspended in this in-coming air had been all deposited in the bend, was conclusively demonstrated by inclining the flask so as to allow a few drops of the liquid to run into the bend where it was soon found to develop growths, thus disposing at the same time of the possible objection that the liquid had been devitalised, as formerly suggested by Needham, in the process of heating.

During the progress of these investigations, Pasteur was continuously

harassed by the publications of his opponents who claimed to have obtained results entirely at variance with his own. This opposition was long endured by Pasteur, but his patience ultimately gave way when some of his experiments were directly challenged by Pouchet, Joly, and Musset, who asserted that in repeating them they had obtained diametrically opposite results. To put an end to this unbearable criticism, Pasteur conceived the idea of settling the dispute by a method which has recently played such an important part in the settlement of a great national dispute of our own, namely *arbitration*. He appealed to the Academy to appoint a special commission to judge between himself and his scientific opponents. Although the recognition of such a tribunal may be regarded as an advantageous method of averting a sanguinary war between two nations without armies, or of preventing a disastrous strike of colliers, dockers or quarrymen, it will, I think, hardly recommend itself as a means of arriving at the truth in a scientific conflict, for in such disputes there is but one Court of Appeal, Time, and the opinion of Posterity. The commission was duly appointed and the method of procedure and result were as remarkable as instructive. It was arranged that both parties should appear at the bar of the Academy and there perform their rival experiments. On the day appointed Pasteur and his assistants arrived laden with apparatus which they were ready at once to put in operation; M. Pouchet and his adherents were there also, but they had come empty-handed. They asked for time, and urged that the weather was unpropitious to the success of their experiments, which had been made at a different season of the year. The commission would not accede to the remand, Pasteur successfully performed his experiments, and a strong judgment was given in his favour (*Ann. Chim. Phys*, 1865, [iv], 4, 353). Before the superior court of Time, however, even the most distinguished Academicians must bend, and we now know that their judgment was wrong, and that Pasteur and his opponents were, in reality, both right as regards what they had observed in their respective experiments, but before such a tribunal obviously nerve as well as right were indispensable for securing justice. The facts are these: Pasteur had used infusion of yeast as the putrescible material in his experiments, Pouchet had used infusion of hay in his; the infusion of yeast is easy, the infusion of hay excessively difficult, to sterilise by heat; the heat applied by Pasteur was sufficient to sterilise the yeast infusion, it would have been insufficient to sterilise the hay; and consequently the heat applied by Pouchet, which was the same as that used by Pasteur, failed to sterilise the hay infusion which he alone employed.

Through the want of confidence in themselves exhibited by Pouchet and his associates in this extraordinary trial, and by the Academic

tribunal giving judgment in default, the knowledge of the whole truth was delayed by some years, for it was not until 1876 that Pasteur's easy triumph over his adversaries was again called in question. Here lies the subtle danger of a body, however distinguished, undertaking responsibilities altogether beyond their real capacity, for doubtless the authoritative pronouncement of the Academy succeeded in protecting Pasteur from his French antagonists, by throttling renewed investigation in the country in which their judgment was final, but fortunately it could not blockade research throughout the world, it could not protect him from attack by scientific foes owning no allegiance to the august body whose aid he had so successfully invoked. The imperfections in Pasteur's methods of that time were in 1876 brought home to himself by the challenge which he received from Dr. Bastian, and it was in repeating *his* experiments and in fighting his erroneous conclusions that Pasteur was led to discover that there exist micro-organisms which are more difficult to destroy by heat than he had before supposed, and that it was the presence of these which had led astray so many zealous experimenters who were too ready to give credence to this chimera of spontaneous generation.

In looking back upon this period of Pasteur's career, one is disposed to regret that his great powers should have been so long absorbed in this work of exterminating a mere superstition, but, as a matter of fact, much good came of this crusade in a number of ways. Incidentally, experiments, which have now become classical, were made on the distribution of micro-organisms in our surroundings, such as air and water, whilst healthy urine and the blood of normal animals were in 1862 and 1863 shown to be free from microbes and capable of being preserved without alteration for an indefinite period of time, provided they were collected with suitable precautions. Van der Broeck had, indeed, already in 1857 and 1858 proved that grape-juice, white and yolk of egg, gall, urine, and arterial blood, if suitably collected, could be preserved without change in their natural condition, whilst subsequently sterile milk in its natural condition was obtained direct from the udder by Roberts, Lister, Cheyne, Meissner, and others. The spontaneous generation controversy was, moreover, highly fertile in developing the general methods of bacteriological research, and many of the most familiar operations employed in the study of micro-organisms date from this period.

It is almost needless to say that the prize offered for researches throwing light on the question of spontaneous generation was awarded to Pasteur, and in 1862, at the age of 40, he was elected a member of the Academy of Sciences.

Studies on the Vinegar Process.

Having temporarily suppressed opposition in the spontaneous generation controversy, Pasteur returned to his fermentation studies, and the interest which his discoveries in this field excited was no longer limited only to the devotees of science, the frequenters of laboratories, and the readers of scientific periodicals, but it began to penetrate that vast assemblage of persons whose main object in life is to obtain the maximum return for capital invested, and who constitute the industrial world. Thus, about this time, we find Pasteur delivering an address to the vinegar manufacturers of Orléans, an address which has since become famous by reason of the important revelations which it contained concerning the production of vinegar by new methods. Pasteur had shown that the conversion of wine into vinegar is the work of a minute rod-like organism, which he called *mycoderma aceti*, the habits and mode of life of which he had so carefully studied that he was able to indicate to these employers of labour the manner in which it ought to be housed, fed, and treated, in order to do the maximum amount of work, in the shortest period of time, and for the lowest possible wage. This *mycoderma aceti* is, indeed, a peculiarly difficult *employé* to deal with, for if supplied with an insufficient allowance of alcohol he revenges himself by consuming the acetic acid which he has been engaged to produce.

As in the case of the alcoholic fermentation, so in that of the vinegar or acetic fermentation, Pasteur was neither the first to discover the process, nor the first to see the living ferment, nor yet even the first to connect the process with the life of the micro-organism. The chemical change involved, and the part played by oxygen in the souring of wine, were already indicated by Lavoisier; the process was ascribed to catalysis by Berzelius in 1829. The skin which forms on the surface of the acetifying liquid was already named *mycoderma* by Persoon, in 1822, and the bacterial cells of which this pellicle is composed were already seen and described by Kützing in 1837 under the name of *ulvina aceti*, and between the life of the latter and the vinegar process a connection was, by him, actually suspected. It will be asked, then, where does Pasteur's discovery of the acetic fermentation come in, when this discovery was already a *fait accompli* at the time when Pasteur was catching fish and drawing caricatures as a schoolboy at Arbois? It is, however, one thing to dream of empire, and another thing to actually found one, so it is one thing to make a discovery and often a very different thing to make the world accept it. It is here that Pasteur stands out in such bold relief from so many other distinguished savants of the century. Just as in connection with the alcoholic fermentation the pioneering work of Cagniard Latour and

Schwann was of such a character that it was practically effaced at one fell swoop by the edict of Liebig, so here again the structure raised by Kützing was within two years demolished by the same autocratic mandate. But whilst the houses built by Cagniard Latour, by Schwann and by Kützing were only founded on sand, and therefore destined to fall almost with the first winter's blast, Pasteur was an architect who built only on the solid rock of experiment, and the many mansions which he has raised on the sites where lie the shattered and almost forgotten ruins of his predecessors have invariably withstood the whips and scorns of time, becoming only mellowed by age. It is in this connection that we realise that Pasteur was not only a savant content to seek the truth and find it, but that when he had in any matter succeeded in the difficult task of convincing himself, he was impelled with almost a fanatic's zeal to force his conviction on the world, nor did he put up his sword until every redoubt of unbelief had been taken, every opponent converted or slain. Of this uncompromising spirit in his championship of what he believed to be the truth he was himself conscious, as is seen from the following passage which occurs in that short reply which he made at that supreme hour of his life when, on attaining the age of 70, he enjoyed a triumph such as has probably never been accorded to a man of science before or since: "Si parfois j'ai troublé le calme de nos Académies par des discussions un peu vives, c'est que je défendais passionnément la vérité." (Jubilée de M. Pasteur, 1892.)

In perusing those terse summaries in which Pasteur's labours on the acetic fermentation are recorded in the *Comptes rendus*,* the reader cannot fail to be struck with the breadth and scope of the view which he takes of the phenomena before him, and the manner in which he shows, by a pregnant word here and there, the alertness of his mind to developments which even now are only partially realised. Thus he points out that these organisms are not only endowed with the power of producing acetic acid from alcohol, but that they can impose the oxidising action of the air on a multitude of organic substances, the sugars, the organic acids, divers alcohols, and albuminoids, giving rise in some cases to intermediate products of which he had already detected some. Here, then, we have indicated those beautiful transformations, carried into execution many years later by Mr. Adrian Brown, in which, by the agency of the acetic bacteria, normal propylic alcohol was made to yield propionic acid, *d*-glucose to give *d*-gluconic acid, mannitol to produce lævulose, and glycol, glycollic acid, whilst methylic, isobutylic, and amylic alcohols, as well as cane-sugar, milk sugar, starch, and dulcite remained unaffected (Trans., 1896, **49**, 172). He further points out the oxidising action possessed in varying degrees

* *Compt. rend.* "Études sur les mycodermes," 1862, **54**, 265 and **55**, 28.

by the family of moulds, and thus shows the path subsequently travelled along by Le Bel and many others in what may be called the *mould-combustion* of racemoids, as well as by Wehmer* in the mould production of oxalic and citric acids from carbohydrates. The same few pages indicate the necessity of reopening the investigation of the process of nitrification, and thus suggest the subsequent successful researches of Schlœsing, Muntz, Warington, Munro, Winogradsky, and others.

These researches on the acetic fermentation open again a new chapter in Pasteur's career, for whilst in his previous investigations he had restricted himself to the purely scientific aspects of the problems on which he was engaged, from henceforward we find the practical application of scientific knowledge occupying a large part of his attention. The success which attended his efforts in thus applying his discoveries doubtless soon led to the growth of a conviction within him that he was entrusted with a great mission, which embraced not only the revelation of abstract truth, but also the promotion of the material welfare both of his own beloved country and of humanity at large.

Thus his excursion into practical matters in connection with the manufacture of vinegar was at once followed by his giving similar attention to questions relating to the production of wine. Already in his writings on vinegar, too, he sounds that note which was soon to become the leading one of his compass; for beginning with '*les maladies du vinaigre*,' he passes to '*les maladies des vins*,' '*les maladies de la bière*,' '*les maladies des vers à soie*,' until he endeavours to extend his healing hand to those numerous ills that are the inheritance of the flesh of man and beast.

The Diseases of Wine.

In placing the vinegar process on a sound scientific basis, Pasteur had obviously, in reality, broached the subject of the '*maladies des vins*,' for that the souring of wine is one of the most widespread ills to which it is subject is surely well known to all possessing even the most modest of cellars. What more natural, therefore, than that Pasteur should conceive that those other and more mysterious deteriorations which wines so frequently undergo might receive a rational explanation by the application of the same methods which had elucidated the vinegar process? Nor were these methods found wanting in dealing with the other diseases of wine, for whilst in healthy or normal wines Pasteur found only yeast cells, in all those wines which connoisseurs condemned as diseased he found other micro-organisms as well, and

* Wehmer, *Beiträge zur Kenntniss einheimischer Pilze. I. Zwei neue Schimmelpilze als Erreger einer Citronensäuregährung.* Hanover, 1893, *Centralbl. f. Bakteriol.*, 1894, **15**, 427.

the nature of these micro-organisms was found to vary according to the complaint with which the wine was charged. Although a number of different bacteria connected with these several maladies of wine were described and figured by Pasteur, it must not be supposed that the mechanism of these processes was investigated with anything like the completeness of the acetification process. The chemical changes taking place are of a much more complex character than that of acetification, and a large amount of work still remains to be done in connection with these more obscure difficulties which attend the production of sound wine. To Pasteur, however, is due the broad explanation of these phenomena as dependent on foreign organisms, and the further elucidation of the subject is chiefly a matter of laborious detail. Nor did Pasteur confine himself to establishing this connection by experiment, but directed his attention to the possibility of guarding against these disturbances.

If these several diseases of wine are due to the presence of living organisms, their radical cure will obviously consist in effecting either the removal, paralysis, or destruction of the mischievous microbes. Pasteur's first efforts were directed to effecting their destruction by means of antiseptics, such as the alkali hypophosphites and bisulphites, but as the results obtained in this manner were unsatisfactory, he resorted to the method of destroying micro-organisms by heat. The thought at once suggests itself that possibly this cure would be worse than the disease, for there is something in the idea of heating wine which does violence to natural instinct. Pasteur had, however, previously very carefully studied the relationship of wine to oxygen, and he did not anticipate that any evil would result provided the wines were only heated after they had finished absorbing oxygen. Moreover, he foresaw that a comparatively low temperature—far below boiling—would suffice, as from his experiments on spontaneous generation he was well aware that the acid reaction of the wine would facilitate the sterilisation, whilst he had further reason to believe that it would not be necessary to actually destroy all micro-organisms, and that it would be quite sufficient only to so paralyse their activity as to prevent their inducing prejudicial changes in the wine. This simple process of partial sterilisation, which was first applied by Pasteur to wine, is now generally known by his name as "pasteurisation," and has already proved of enormous value to man, having been employed with the greatest success in connection with wine, beer, milk, cream, and other food materials of a perishable nature, whilst in the future, I believe, it is destined to become of ever increasing importance. The wholesale abuse of antiseptics in this country at the present day must lead to a reaction before very long, for it is rapidly coming to this, that there is hardly a purchasable article of food which is not tainted

with the suspicion of being mixed with some preservative which, whilst harmless enough when taken occasionally in small quantity, may not improbably lead to grave disturbances if habitually made to form part of almost every meal during a lifetime. In other countries where Governments consider it necessary to keep themselves, to some extent at least, in touch with the progress of science, many of these preservatives are prohibited by laws which bear only one meaning, whilst with us almost every protective enactment is so framed as to admit of a different interpretation by every local magistrate and by every British juryman. When the present darkness has given place to light, it is to be anticipated that the preservation of perishable food materials by Pasteurisation will supersede the present methods of preservation by poisons.

Controversy with Liebig.

It was thus by a long line of monumental researches that Pasteur had established the vitalistic theory of fermentation, which may be summarised in the words:

No fermentation without organisms; for each kind of fermentation a particular organism.

It was hardly to be expected that Pasteur's opponents would allow this theory to triumph without striking a last blow in defence of the chemical or molecular vibration theory, which had enjoyed such a long supremacy over the vitalistic theories of thirty years before. Accordingly, in 1869 we find Liebig making a lengthy communication to the Munich Academy, under the title of "On Fermentation and the Source of Muscular Power." The paper is of psychological rather than scientific interest, the reader having little difficulty in discerning that the great chemist, in the winter of his brilliant career, is trying to retreat in good order before the irresistible advance of the younger man with his improved weapons of precision, and to cloak his defeat by endeavouring to show that there is but little real difference between the two interpretations put on fermentation phenomena. But towards the end of the paper there is a sudden change of tone, for the author, doubtless so well satisfied with his execution of the retrograde movement, has deceived himself as to the real nature of his position, and when he should have been content to decently bury an obsolete cause he becomes once more aggressive and contemptuous. He denies the activity of the *mycoderma aceti* on the beechwood shavings used in the German vinegar process, and calls to his assistance in this weighty charge the *ipse dixit* of a worthy Munich vinegar manufacturer of the name of Riemerschmied. He challenges the accuracy of Pasteur's observation that yeast can find its nitrogenous nutriment in ammonia, and suggests that his results are due to analytical inaccuracy. In

support of his disbelief in the assimilability of ammoniacal nitrogen, he invokes the assistance of vegetable physiology—which then denied to all but green plants the power of building up albuminoids from ammonia. But the scientific world had yet to learn how often vegetable physiology would have to change its foliage at the bidding of Pasteur and his successors. What would Liebig have said had he been told that the study of these micro-organisms for which he cannot disguise that contempt which has been shared by so many chemists even up to within the last few years, would within the century reveal the fact that carbonic acid can serve as a source of carbon to plants without chlorophyll, and that albuminoids can be synthesised from the free nitrogen of the air?

The reply did not come until after the war of 1870, and the effect of that *débacle* on Pasteur, who was even a greater patriot than savant, cannot be realised by Englishmen who for generations have not seen an enemy on their own soil.

To my mind, this reply appears a masterpiece of self-restraint, considering the circumstances of intense irritation under which it must have been written. Terse, and to the point, the few pages of Pasteur's reply form a most welcome contrast to the verbose and unwieldy document of the Teutonic veteran. Without wasting time on the sterile disquisition of which Liebig's paper is mainly composed, he hastens to fall like a sledge-hammer on the two direct negatives with which he had been challenged, namely, (1), the assimilability of ammoniacal nitrogen by yeast, and (2), the participation of the *mycoderma aceti* in the German vinegar process. After reasserting the correctness of his previous statements, he exclaims:

"Mais comment éclairer le public? Comment sortir de l'embarras que soulèvent ces affirmations contradictoires également honorables?"

Then he has recourse to those tactics which he found so effective in the case of his dispute with M. Pouchet, by calling on Liebig to submit his difference to the arbitration of the Academy, he (Pasteur) undertaking to prepare several kilograms of yeast from purely mineral materials, and also to satisfy by ocular demonstration both Liebig and the Academic Committee that the beechwood shavings in Herr Reimerschmied's vinegar factory were covered with growths of the *mycodermi aceti* which Liebig had been unable to discover. The same success attended this move of Pasteur's as on the previous occasion, for Liebig did not accept the challenge, and with his failure to do so fell also the theory by championing which he had succeeded in stopping the clock of the fermentation world over a period of nearly thirty years.

The war of 1870 plunged Pasteur into the very deepest melancholy and despair. As I have said before, he was perhaps even more patriot than man of science, and the condition of his mind at this crisis is

most vividly illustrated by the following letter which, after the bombardment of Paris, he addressed to the Dean of the Medical Faculty at Bonn:

"Arbois (Jura), 18*th January*, 1871.

"Monsieur le Doyen,

"In 1868, the Faculty of Medicine of the University of Bonn did me the honour of bestowing on me the degree of Doctor of Medicine, in recognition of my labours on fermentation and on the part played by microscopic organisms. Of all the distinctions which my researches during the past twenty-two years have brought me, I admit that there is not one which has given me more satisfaction. . . ."

After referring to the fact that he had framed the diploma and hung it up in his study, he says:

"To-day, the sight of this parchment is odious to me, and I feel offended at seeing my name, with the qualification of *virum clarissimum* which you have bestowed upon it, placed under the patronage of a name doomed henceforward to execration by my country, that of *Rex Guilelmus*.

"Tout en protestant hautement de mon profond respect envers vous et envers tous les professeurs célèbres qui ont apposé leur signature au bas de la décision des membres de votre ordre, j'obéis à un cri de ma conscience en venant vous prier de rayer mon nom des archives de votre Faculté et de reprendre ce diplôme en signe de l'indignation qu'inspirent à un savant français la barbarie et l'hypocrisie de celui qui, pour satisfaire un orgueil criminel, s'obstine dans le massacre de deux grands peuples."

. . . . . .

The practical outcome of this patriotic sentiment so highly developed in Pasteur was that he undertook those famous researches on beer which were commenced within a few months after the cessation of the roar of the German artillery around the walls of Paris, and which had for their object such an illumination of the brewing industry as would enable France to produce malt liquors of equal value and excellence to those for which her hereditary enemy across the Rhine had so long been preëminent:

"L'idée de ces recherches m'a été inspiré par nos malheurs. Je les ai entreprises aussitôt après la guerre de 1870 et poursuivies sans relâche depuis cette époque, avec la résolution de les mener assez loin pour marquer d'un progrès durable une industrie dans laquelle l'Allemagne nous est supérieure." (Preface to *Études sur la Bière*, 1876.)

These researches were in 1876 collected and printed in a single volume bearing the title of *Études sur la Bière*, which is unquestionably the best known of all Pasteur's publications in this country and which has been translated into English. I do not know whether this work has been consulted by the great titled millionaires of the brewing world, or even whether it is to be found in their libraries, but I do know that

it has for twenty years served as a gospel to those members of our profession who are the brains and right hands of the great brewing concerns of this country. I say "gospel" and not "law," as it is rather by the spirit which it breathes than by the letter itself that it has proved of such inestimable value to those engaged in the solution of fermentation problems.

From a chemical point of view, the centre of gravity of the *Études sur la Bière* is undoubtedly the new theory of fermentation which it contains, and which may be summarised in the words "Fermentation is life without oxygen."

To the enunciation of this theory, Pasteur was led by a careful study of the phenomena exhibited on the one hand by the life of aërobic organisms in the absence of air, and on the other hand of anaërobic organisms in the presence of air. "*La fermentation est la conséquence de la vie sans air*" (p. 271).

It had been asserted in 1857 by Bail that the mould, *mucor mucedo*, which is so common on horse-manure, becomes transformed into brewer's yeast if grown out of contact with air by immersion in a saccharine liquid, and that the latter under these conditions suffers the ordinary alcoholic fermentation. Pasteur repeated this experiment, using special precautions, and was able to confirm the apparent transformation and the alcoholic fermentation consequent thereon. He, however, showed that the round or oval cells obtained were not veritable yeast, but that they only simulated the latter, and that the change in form was only a concomitant of the change in function under the altered conditions of life, for on bringing these yeast-like cells to the surface they again gave rise to an ordinary mould mycelium which destroyed the sugar by oxidation. The power of decomposing the sugar into alcohol and carbonic anhydride is thus only possessed by the *mucor mucedo* as long as it is growing in the absence of air, or, in other words, the *mucor mucedo* becomes a ferment when deprived of oxygen. (See also Emmerling, *Ber.*, 1897, **30**, 454.)

Pasteur has endeavoured to trace the counterpart of these phenomena in the behaviour of ordinary yeast when grown in the presence and absence of air respectively.

Thus he found that yeast could grow in the absence of air, and although the growth was a very feeble one, and the absolute amount of sugar transformed into alcohol and carbonic acid very small, yet the weight of sugar so transformed per unit weight of yeast present was very large indeed (176 of sugar : 1 of yeast). On the other hand, by admitting a small quantity of oxygen, the growth of yeast is more abundant and the fermentation accelerated, but the transformation of sugar for unit weight of yeast present is less than in the entire absence of oxygen (76 of sugar : 1 of yeast). By further increasing

the quantity of oxygen, the disappearance of the sugar is still more rapid and the growth of yeast still more abundant, but there is hardly any alcohol formed, the sugar having principally suffered oxidation instead of decomposition; moreover, the amount of sugar which has disappeared per unit weight of yeast present is still lower than in the previous case (4 of sugar : 1 of yeast). (*Études sur la Bière*, 237, 241, 244.)

It is these and other results of a similar character which Pasteur cites in support of his theory that fermentation is life without air. Thus, defining the fermenting power or "pouvoir ferment" as the amount of sugar transformed by unit weight of yeast, he points out that the value of this power increases in the absence of air and decreases in its presence, as indicated by the experimental figures which I have quoted.

The importance of this conception, *pouvoir ferment*, was questioned already at the time, in 1875, by Schützenberger (Schützenberger, *Les Fermentations*, 1875), who considers that the really vital factor is the amount of sugar transformed by unit weight of yeast in unit of time, and this has been again quite recently urged by Mr. Adrian Brown (*Centralbl. f. Bakteriologie* (II. Abth.), vol. 3, 33; Trans., 65, 911), who maintains that in the measurement of any work performed by an organism the element of time must be taken into consideration. Mr. Brown, in fact, denies that Pasteur's experiments, which I have summarised above, have any real bearing on this theory, because the times occupied in the several fermentations were utterly different, thus, whilst the fermentation without any air was continued over three months, that in which most air was present was terminated in a few hours.

Mr. Adrian Brown is therefore anxious to ascertain whether unit weight of yeast is decomposing more sugar in unit of time when it is supplied with air or when it is deprived of air, and this information the experiments in question do not furnish, because the quantity of yeast is changing throughout the course of each experiment, and the rate of change is different in the different experiments.

Mr. Adrian Brown has endeavoured to solve this problem in a very ingenious and original manner, by taking advantage of an interesting discovery which he has made with regard to the multiplication of yeast. Thus, Mr. Brown finds that, in a given saccharine solution, yeast will multiply until there is a certain number of cells per unit volume of liquid (Trans., 1892, 61, 370), and that when this maximum has been reached reproduction ceases. The existence of such a maximum obviously opens up the possibility of studying the decomposition of sugar by yeast in the absence of yeast reproduction. This is what has been done by Brown; yeast cells in excess of the ascertained

maximum were introduced into a saccharine liquid, one-half of this was supplied with air, the other half was protected from the air, and the experiments, which were varied in a number of different ways, in all cases yielded the same result, namely, that in a given time a given number of yeast cells, *undergoing no multiplication*, decomposed slightly but distinctly more sugar in the presence than in the absence of air. Thus in the absence of yeast reproduction, it would appear that one yeast cell decomposes more sugar in unit time in the presence than in the absence of air. But there is the further point to be taken into consideration that, as Pasteur pointed out, the sugar may be decomposed by the yeast in two different ways, namely, first, by what we may call fermentation, that is, with production of alcohol and carbonic anhydride, and, secondly, by complete oxidation after the fashion of moulds; now in the great majority of these researches on yeast fermentation it is the destruction of sugar that has been alone determined, the nature of the products formed having been left out of consideration.* It is obviously quite possible that a yeast cell may be decomposing in a given time a large amount of sugar, but if the decomposition is wholly by way of oxidation, that yeast cell would not be acting as a *ferment* at all, at any rate in the sense that the word is used by Pasteur.

The following facts would appear, then, to be established.

(1) From Pasteur's experiments, on the one hand, we know that a single yeast cell, growing in a saccharine liquid until a ponderable quantity of yeast has been produced, decomposes more sugar, per unit weight of yeast formed, in the absence than in the presence of air.

(2) From Adrian Brown's experiments, on the other hand, we know that a single yeast cell undergoing no multiplication decomposes slightly more sugar in unit of time in the presence than in the absence of air.

It is, however, obvious that, even if more sugar is fermented by yeast in the presence than in the absence of air, there is nothing in this antagonistic to Pasteur's theory that fermentation is the consequence of life without air, for surely the decomposition of the sugar into alcohol and carbonic anhydride may still be a vital action which is qualitatively independent of air, and which is only quantitatively dependent on the presence of air in so far as the general vitality of the yeast cell is stimulated by aëration. Moreover, even Adrian Brown's experiments show that the decomposition of sugar is quantitatively but little affected by the entire absence of air provided no yeast-multiplication is permitted. It is, in fact, quite conceivable that the yeast cell may be stimulated by the presence of air, and yet that

* This has recently been attempted by Giltay and Aberson. Pringsheim's *Jahrbuch. f. wissensch. Botanik*, **27**, 543; see also *Ann. de l'Inst. Pasteur*, **10**, 183.

practically the whole of its vital processes are carried on without the participation of the free oxygen, provided sugar be present; and we know that these processes *can* be carried on without air in a saccharine liquid. In short, the energy required for the life of the yeast may be derived from the decomposition of the sugar and not from oxidation processes effected by free oxygen. It is this capacity to utilise the energy locked up in the sugar, and which is set free when the sugar decomposes into alcohol and carbonic anhydride, which entitles the yeast to the name of *ferment* according to Pasteur's definition.

Before dismissing this subject of Pasteur's fermentation theory, which, it is to be hoped, will still continue to stimulate research in the future as it has done in the past, I would refer to two very remarkable confirmations adduced by Pasteur in support of his theory (*Études sur la Bière*, 248). Firstly, in connection with industrial practice; where the production of yeast is the object of the manufacturer, the liquids in which the yeast is grown are kept as fully aërated as possible, experience showing that thus the maximum transformation of sugar into yeast cells is secured. Secondly, the discovery in 1869 by Lechartier and Bellamy (*Compt. rend.*, 1869, 69, 366, 466), that the vegetable cells present in ripe fruits transform a part of the sugar which they contain into alcohol if the fruits in question are preserved in an atmosphere of carbonic anhydride, would tend to show that the production of alcohol from sugar is a more or less general property of vegetable protoplasm when deprived of free oxygen, irrespective of the nature of the cells in which this protoplasm is contained. Similarly, as we have seen, the protoplasm of the mould *mucor mucedo*, under ordinary circumstances, that is, in the presence of air, does not decompose sugar with formation of alcohol, but only exhibits this power when it is deprived of free oxygen.

The whole question should assume a different aspect now that we appear by E. Buchner to have been put in possession of the enzyme giving rise to the alcoholic fermentation of sugar. It will now be possible also to attack the problem in a new and much more decisive manner. Thus it is presumably very improbable that the action of the enzyme is influenced by the presence or absence of air, but it is very possible that the amount of enzyme produced in a given yeast cell may depend largely on whether the latter is supplied with or deprived of free oxygen. These are points on which we may hope to have definite information before long.

I should, however, only be conveying a very imperfect idea of the importance of Pasteur's work on fermentation were I to omit to mention its influence in directions which at first sight have very little connection with fermentation and the great industries which are dependent on the application of these processes. I refer, of course, to

the immediate influence which Pasteur's fermentation researches exerted in the domains of medicine, surgery, and public health. Pasteur was fully convinced of the possibility of extending the great principles which he had established in connection with fermentation to the phenomena of disease, but he was filled with well founded anxiety lest, through exaggerated statements and undue haste in drawing conclusions, a reaction should be provoked and that the new ideas should fall into disfavour.

It was in this direction that he feared the doctors especially would err, and it is this apprehension which leads him to make the following remarks about the members of the medical profession:

"Malheureusement les médecins se plaisent volontiers dans les généralisations anticipées. Beaucoup d'entre eux sont des hommes d'une rare distinction naturelle ou acquise, doués d'une intelligence vive, d'une parole élégante et facile; mais plus ils sont éminents, plus l'art les absorbe et moins ils ont de loisirs pour le travail d'investigation. Poussés, néanmoins, par la passion du savoir, propre aux esprits d'élite, et qu'entretiennent les relations de la haute société de plus en plus curieuse des choses de la Science, ils s'emparent avidement des théories faciles, spécieuses, d'autant plus générales et appropriées aux explications vagues qu'elles sont mal établies par les faits." (*Études sur la Bière*, 41.)

Amongst a number of achievements in medicine and surgery to which Pasteur refers as having been ascribed by their authors to the influence of his fermentation studies, he singles out with special pride, and reproduces in full, as affording him the greatest satisfaction of all, a letter addressed to him in 1874, "par le célèbre chirurgien d'Edimbourg, le Dr. Lister"; and by so doing Pasteur shows how incomparably clearer was his insight into matters medical than that of the profession itself, realising, as he did already then, that the departure which is associated with the name of the President of the Royal Society was by far the most important application of his researches on fermentation. For how true are the words contained in the recent medical estimate of Pasteur's work by M. Roux (Roux, *Agenda du Chimiste*, 1896, 528):

"Éclairé par les expériences de Pasteur, Lister comprend que les complications des plaies sont dues aux germes microbiens venus du dehors et il imagine les pansements antiseptiques. Avec l'antiseptie commencent les temps nouveaux de la chirurgie. C'est grâce à une expérience bien faite sur la fermentation que Pasteur, qui de sa vie n'a tenu un bistouri, ni fait un pansement, a sauvé plus de blessés que tous les maîtres de la chirurgie."

Silkworm Diseases.

Before entering on the last chapter in Pasteur's career, in which he determines personally to follow out the pathological developments of

his fermentation studies, we must turn our attention for a few minutes to an incidental investigation into which he was, so to speak, forced by his superiors, and which proved an admirable preparatory school for those great final labours on micro-organisms and disease which have rendered his name a household word throughout the civilised world.

In 1865, the silkworm culture, which forms such an important industry in the South of France, was threatened with ruin in consequence of a most disastrous disease having made its appearance amongst the worms. The Government was appealed to for assistance, and it might have been supposed that they would, under the circumstances, have applied for advice to some distinguished zoologist, entomologist, or other authority learned in the ecdyses and metamorphoses of the Insecta in general and of the Lepidoptera in particular. With admirable sagacity and courage, however, they ignored the very existence of the several biological societies, and entrusted the investigation to a man absolutely ignorant of invertebrate anatomy, and who had never even handled a silkworm in his life. It was, moreover, in vain that Pasteur pleaded this ignorance as testifying to his incapacity to undertake the work. "Tant mieux!" said M. Dumas, by whom he had been approached, "vous n'aurez d'idées que celles qui vous viendront de vos propres observations!" (Duclaux, *Histoire d'un Esprit*, 193.)

It must not be supposed that Pasteur was breaking untrodden ground in undertaking this investigation; a mass of literature already existed on the subject, a great number of careful observations had already been made. Microscopic corpuscles had been seen in the diseased silkworms by Guérin-Menneville; their pathological import had been suspected by Cornalia; their abundant presence in all the diseased larvæ and moths had been observed by Lebert and Frey, whilst Osimo had found them even in the eggs. Notwithstanding, all remedial measures had proved highly uncertain and often altogether ineffectual. The previously ascertained facts were confirmed by Pasteur, yet nothing is more remarkable than that he, who in his fermentation experiments had been guided by the conviction that the living organism was the cause of the chemical process, should for several years have failed to recognise that these living corpuscles were the real *materies morbi* of the Pébrine, as this silkworm malady was designated, but that, on the contrary, he should have supposed that they were only a consequence of the disease, and therefore a delicate means of detecting its presence. The remedy which he suggested was, however, sound, although based upon this erroneous hypothesis, and consisted in collecting the eggs laid by each moth separately, and then preserving only those which were derived from a male and female moth both of which on microscopic examination had been found to be free from cor-

puscles. Foreseeing that the use of the microscope would prove an impediment to this remedy being adopted by the good people engaged in silkworm culture, he says to them :

"If you tell me that you are afraid of the microscope and that its management does not appear easy, know that I have a little girl but 8 years old who makes very good use of it."

But, in 1867, after having completely elucidated the fatal pébrine both in its theoretical and practical aspects, Pasteur was exposed to the intense mortification of receiving by every post letters loudly complaining of silkworm disease, notwithstanding the adoption of his protective measures, and M. Duclaux, who assisted him throughout this laborious investigation, has described how one morning Pasteur came into the laboratory almost with tears in his eyes, and after falling into a chair disconsolately exclaimed, "Il n'y a rien de fait ; il y a deux maladies !"

Yes, there were indeed two silkworm diseases, and it was their superposition which was largely responsible for the circumstance that Pasteur so tardily arrived at the truth with regard to the corpuscular cause of the pébrine.

Having thus successfully combated this first evil, the pébrine, he was now confronted with a second, the "maladie des morts-flats" or "flacherie," as it is generally called. In studying this disease, which he showed to be of bacterial origin, he was brought in contact with a number of phenomena akin to those which obtain in the infectious diseases of man and the higher animals, and it was in investigating this sort of silkworm cholera, as I may call it, that he acquired a great store of ideas which he afterwards so successfully deployed into line in his brilliant attack on those subtle maladies which absorbed his energies in the later years of his life.*

That he himself was deeply conscious of the educational value which these researches on pébrine and flacherie had possessed for him, is shown by the fact, which M. Roux relates, that in after years, when young medical men were aspiring to undertake pathological researches in his renowned laboratory at the Institut, he never failed to say to them, "Lisez les études sur les vers à soie ; cela sera, je crois, une bonne préparation aux travaux que nous allons entreprendre."

Pathological Researches.

Pasteur's introduction to pathological phenomena in the shape of the silkworm diseases was spread over upwards of five years, 1865—70,

* It is worthy of note that, in investigating the bacteria of flacherie, Pasteur found that they gave rise to oval bodies possessing a high degree of resistance ; this is the first instance in which *spores* were discovered in connection with a pathogenic micro-organism.

and it was during this period of time, namely, in 1868, that he suffered from that paralytic attack which so nearly deprived science of some of the most remarkable discoveries of the last quarter of a century. The physical effects of this seizure Pasteur never shook off, but after a partial retirement extending over two years he was able to resume his labours, and that his mental vigour was not impaired by this terrible visitation is sufficiently obvious from the monumental achievements which followed. Hardly, however, had he recovered from his illness and taken up the threads of his previous researches before the deluge passed over him once more, this time in the shape of the disastrous war of 1870, which, as we have seen, affected him more painfully than it is possible for us to realise. The war over, his invincible energy returning led him to undertake the *Etudes sur la Bière*, of which I have already endeavoured to give some outline, and in which we have seen that his mind was becoming more and more occupied with the analogies subsisting between the phenomena of fermentation and those of disease.

The impulse to undertake himself, and not merely to inspire the investigation of these morbid phenomena, became more and more dominant, until, in 1877, he yielded to its imperious bidding and embarked at the age of fifty-five on that course of pathological study from which he never swerved, and which was destined to make such an epoch in the scientific history of our times.

The problem to which Pasteur first directed his attention in this new field had already attracted a number of investigators, amongst whom were a few men of the very highest ability. In the well-known infectious cattle disease called anthrax, Rayer and Davaine had already, in 1850, pointed out that microscopic, thread-like bodies were discoverable in the blood of the victims, but the importance of this discovery, like that of Cagniard Latour and Schwann in connection with fermentation, did not receive recognition, but was stifled by the "*Zeitgeist*," which had been created in physiology and medicine by the brilliant researches of Helmholtz, Ludwig, Brücke, Dubois Reymond, and Virchow, in the same way as the significance of the yeast cell had been swamped by the mighty torrent of discoveries in pure chemistry. These filiform bodies were again seen and emphasised in 1855 by Pollender, but immediately afterwards brought into discredit by Brauell, only to be again rehabilitated in 1860 by Delafond, who first succeeded in cultivating them in blood outside the body. In 1863, Davaine, prompted by Pasteur's work on the butyric ferment, returned to his researches on anthrax and demonstrated that the blood of animals affected with anthrax could only communicate the disease when these rod-like bodies were present in it, and that if they were removed by filtration, for example, it was incapable of producing infection. It

was, moreover, in the study of this anthrax disease that the greatest living master of pathological bacteriology made his *début*; for, in 1876, Robert Koch, then a humble *Kreisphysikus* in an obscure part of Germany, announced that he too had seen these rod-like forms, that he had succeeded in cultivating them through a number of generations in blood serum and in aqueous humour, and, most important of all, that he had observed their mode of multiplication under the microscope, and had seen that they effected their reproduction, not only by fission, but also by the formation of spores, the incredible vitality of which he had demonstrated by actual experiment, showing that they "in kaum glaublicher Art und Weise ausdauern." The importance of these spores in the etiology of anthrax he had further indicated by showing that they could lead to the infection of animals through the alimentary tract. A series of investigations, therefore, as remarkable for their completeness and convincing force as for the extreme simplicity and beauty of the technique by means of which they were carried out, and sharply foreshadowing the magnificent work which was to follow from the same source.

But, convincing as the proofs furnished by Davaine and by Koch appear to us to-day, they stood in much need of corroboration and extension at the time, for, as those of us who can look back twenty years into the past can well remember, it was with principalities of prejudice and with mighty powers of darkness that the new views concerning the bacterial causes of disease had to contend, and it has, doubtless, facilitated the victory of truth over the strongholds of effete, but all the more obstinate, tradition, that the assault was conducted by two independent schools of bacteriological research, the French and the German, each of which was stimulated to the highest pitch of activity by the fierce rivalry which long subsisted between them.

Of the greatest value, therefore, in carrying conviction were Pasteur and Joubert's new and independent experiments on anthrax, in which all the previous experience gained in the study of fermentations and in that of the silkworm diseases was brought into play. Thus the cultivation of the anthrax bacillus in large volumes of liquid media, and over such a number of generations that the original morbid material taken was diluted to the same extent as would be a single drop added to the ocean, finally disposed of the lingering idea that infection was carried, not by the bacilli, but by an amorphous virus present in the blood of the diseased animal.

Again, as is so frequently the case in repeating and perfecting the experiments of others, new discoveries of the highest importance were made by Pasteur. It was thus that, in repeating the investigations of Jaillard and Leplat, which, some years previously, had so much damaged the bacterial explanation of anthrax, Pasteur, Joubert, and

Chamberland came upon the well-known *vibrion séptique*, now more commonly known as the bacillus of malignant œdema, an organism giving rise to a deadly septicæmia, and which, in its anaërobic mode of life much resembles the butyric ferment which Pasteur had so successfully studied in 1861. It was further shown that, by inoculating harmless bacteria along with the anthrax bacillus, the latter may fail to produce its effect, a discovery which opens out a vista of possibilities which have, even yet, been hardly investigated.

Another classical experiment belonging to this period strikingly illustrates the fertility of Pasteur's imagination and the extraordinary good fortune which attended his speculations. It was known that birds are absolutely insusceptible to anthrax; this circumstance he was led to associate with their high blood temperature, namely, 42°. I think most persons would have dismissed this idea as a passing fancy, but Pasteur submits it to direct experiment; he reduces the temperature of a fowl to 38° by immersing its feet and hindquarters in water kept at 25°, and finds that, on inoculation, it now contracts anthrax, from which it can be made to recover by allowing it to gain its normal temperature. It has been subsequently shown by Gibier that, by raising the body temperature of frogs by means of warm water, these normally insusceptible amphibians can be made to contract anthrax.

Having thus turned his attention to these pathological researches, he casts about him in all directions for material. He walks the hospitals armed with sterile vessels for the collection of morbid products, heroically overcoming the natural antipathy of a sensitive nature to the sight of suffering and distress; he cultivates the *staphylococcus pyogenes* from boils on the person of one of his assistants, M. Duclaux, and from its appearance and characters boldly asserts its identity with the organism found in cases of osteomyelitis; he visits the Maternity Hospital and discovers the *streptococcus pyogenes*, asserting it to be the cause of puerperal fever. In connection with this discovery, an instructive incident is related by M. Roux (*Agenda du Chimiste*, 1896, 536):

"One day, at a discussion on puerperal fever which was taking place at the Academy of Medicine, while one of the most distinguished authorities was eloquently descanting on the causes of epidemics of this disease at maternity hospitals, he was suddenly interrupted by Pasteur: 'ce qui cause l'épidémie, ce n'est rien de tout cela: c'est le médecin et son personnel qui transportent le microbe d'une femme malade à une femme saine.' And when the speaker replied that he was much afraid they would never discover that microbe Pasteur rushed to the blackboard and drew the streptococcus, saying 'Tenez voici sa figure.'"

The surprise, the stupefaction which this assurance of the novice in

pathological study caused amongst the assembly of learned doctors, is more easily conceived than described.

There can be no doubt that the great fertility of Pasteur's researches in so many different departments of science was due to his at once seizing on the essential point of a question, and that he always directed his attention to the main line of an enquiry, without allowing his time and energies to be frittered away by side issues and considerations of secondary importance. Thus, as we have so frequently seen, whilst there was no detail so insignificant as to escape his observation, yet these details were at once sifted by him, and only those which were of importance to his train of thought followed up. In fact, he entered the most widely different departments of knowledge, not because of his special interest in each, but only because the logical sequence of his ideas necessitated his passing from the one to the other. Thus in his biological studies he was utterly indifferent to those purely morphological questions in which so many investigators in this branch of science appear to find a permanent anchorage, and an incident is related by M. Duclaux of an able morphologist who came to the laboratory one day and explained to Pasteur in the most courteous terms that a particular organism which he (Pasteur) had described as a micrococcus was in reality a small bacillus, information of such vital importance to the microscopist, which only evoked the brusque reply, "*Si vous saviez combien cela m'est égal!*" (*Histoire d'un Esprit*, 316); a remark which very clearly indicates his attitude of mind and his power of dissociating the essential from the non-essential, his discrimination between the things which belong to nature and the things which are the outcome of the vanity of man.

Attenuation of Virus.

The occupation of discovering pathogenic bacteria, fascinating as it was, could not permanently engross Pasteur's attention, and his winged fancy rapidly soared beyond the mere etiology of disease. His mind's eye had long been riveted on that great achievement of Jenner's which towers in royal isolation above the plains of the medical history of centuries, an achievement which, as Herbert Spencer has pointed out, a grateful country has up to the present rewarded by a begrimed statue hidden away in an obscure corner of Kensington Gardens frequented chiefly by nursemaids and perambulators. The thought ever present in Pasteur's mind was to secure an immunity from those diseases for which the nature of the viruses had now been made known, similar to that which Jenner had secured in the case of a disease of which the virus is of so subtle a nature that it even still baffles the most modern methods of investigation. This

new ambition was destined to be soon realised through one of those events which, when occurring singly, appear to be wholly due to chance, but which when recurring again and again in connection with one and the same individual are the most unmistakable evidence of genius.

All who have seriously worked with bacteria must have experienced the difficulties which stand in the way of taking any prolonged holiday; to the chemist the vacation often comes as a welcome assistant in his researches; refractory oils and unpromising syrups which are set aside almost in despair at the end of the term often greet us on our return to work with crystalline forms which gladden the eye and make the heart beat with redoubled vigour at the prospect of renewing our labours, but the bacteriologist returns after a hardly earned holiday only to find that the cultivations, which have perhaps taken him months or even years to obtain, are languishing or even defunct through the want of that maternal care which he was wont to lavish on them, or that they have suffered contamination while consigned to the stepmotherly care of some unworthy assistant.

It was thus, in 1879, that, on returning from a holiday, which had interrupted Pasteur's researches on fowl cholera, he found all his cultivations of the microbe of this disease either dead or nearly so, and that many of the animals which he inoculated with these exhausted cultures continued to roam about their cages in apparent health and comfort instead of being stricken down with the malady from which before there had been no reprieve. Having ultimately again obtained a virulent culture, the idea occurred to him of re-inoculating the birds which had survived the previous treatment with the exhausted cultures, and what was his astonishment on seeing that these birds resisted the attack of the virulent organisms which proved rapidly fatal to those which had undergone no previous inoculation with the exhausted cultures. Here, then, was at last, after the lapse of nearly a century, a sequel to Jenner's great discovery of vaccination, but a sequel with this important difference, that whilst Jenner's vaccine for human smallpox was produced in the living tissues of another animal, the vaccine for fowl cholera was produced in an artificial cultivation contained in a glass vessel.

It must be noted that to this discovery were added several highly important principles, thus, firstly, that it is possible by suitable treatment to diminish or '*attenuate*' the virulence of a pathogenic organism to any desired degree; secondly, that this attenuated virulence is hereditary and can be propagated through practically an almost unlimited series of generations without alteration; and, thirdly, that the milder type of malady which follows upon inoculation of such an attenuated virus or 'vaccine' is capable of protecting the animal from subsequent attacks of the virulent microbes of the same species. Moreover, this

protection is the more complete the more virulent the vaccine and the more recently it has been employed.

Similarly, graduated vaccines were obtained of the anthrax bacillus, and of the microbe giving rise to the malady affecting swine and known as *Rouget de porc*, or swine measles.

The simple method of producing a vaccine which had proved so successful in the case of fowl cholera had to be slightly modified in the case of anthrax, for whilst the anthrax bacilli similarly suffer diminution in virulence through ageing, the spores do not, their virulence being practically unaffected by time. It was necessary, therefore, to produce the anthrax vaccine by the ageing of a cultivation wholly free from spores, and this it was found could be done by keeping the culture at 42—43°, at which temperature no spores are formed, and according to the length of time to which the cultures are thus exposed, more and more attenuated viruses or vaccines of anthrax are obtained.

The successful preparation of a vaccine for anthrax was not merely of theoretical interest, as was that for fowl cholera, and it was, after several public demonstrations of its efficacy which I have not time to describe, put into practice on a large scale, in connection with which I would only refer to the statistics published by M. Chamberland in 1894. During the previous ten years there had been vaccinated for anthrax—

3,400,000 sheep . . with a mortality of 1 per cent.
438,000 horned cattle with a mortality of 3 per mille.

From these figures, the gain to the French farmer is estimated at

5,000,000 francs for the sheep
2,000,000 francs for the horned cattle.

And inasmuch as England is particularly rich in individuals who have neither the instinct nor the education to appraise the value of scientific achievements according to any other standard than that of the coin of the realm, I would for their benefit point out that this single discovery of Pasteur's has meant a gain to his country in 10 years of £280,000 sterling.

Science, however, obviously demands an answer to the question whether the converse process can also be realised; that is to say, whether a micro-organism can be artificially rendered more virulent. Pasteur furnished the answer to this question, in 1881 (*Compt. rend.*, 92, 433), by showing that the anthrax bacillus, after being almost wholly deprived of its virulence, could become again endowed with all its former activity by inoculating it into the most tender and susceptible of animals, such as a mouse a day old. With the blood of this victim a somewhat older mouse is inoculated, and so on; passing then from

adult mice to guinea pigs, and from these to rabbits, sheep, and finally to the most refractory animals in succession, the highest degree of virulence can be again obtained. These results, which might at first sight appear to be of purely scientific interest, have in due time been found also of enormous practical importance.

Rabies.

But, as is so well known, Pasteur's researches in this direction were not limited to the attenuation of viruses as a means of preventing disease in animals only, his beneficent investigations were finally extended also to combating disease in man himself. These last labours, moreover, display in their highest degree those remarkable qualities which had characterised his whole career, and for the performance of these labours the powers and experience gained during nearly forty years of ceaseless scientific activity were called into requisition and submitted to the severest strain.

It has appeared a most unaccountable circumstance to many that, in approaching the diseases of man, Pasteur should have made the selection which he did in taking hydrophobia as the first human malady to which he was determined to apply those prophylactic measures which had been found so successful in combating some of the diseases of animals. Thus, terrible as hydrophobia may be to the individual afflicted, it is of little absolute importance to the human race in general, claiming, as it does, perhaps a smaller number of victims annually than almost any other well-recognised malady.

I cannot help thinking that, in making this selection, Pasteur was guided by that instinct which leads the experimental genius to choose those subjects of research which are ripest for attack at the time, and quite irrespectively of their immediate importance to the world in general. Experience has, in fact, fully demonstrated the wisdom of his selection of this comparatively obscure disease as the one on which to make the first assault with the scientific weapons which his researches on fowl cholera and anthrax had created.

The wisdom of his selection doubtless depends on rabies being a well-defined disease in both animals and man, and that it can, therefore, be fully investigated by direct and real experiment on animals, and not merely by those statistical methods which have, in general, to pass muster as experiments in medicine. I venture to think that there is the more force in these remarks, from the fact that so much success has attended this attack on hydrophobia, in spite of our being even still in complete darkness as to the real nature of the exciting cause of the disease, for not only has the microbe of rabies remained undiscovered up to the present day, but rabies is not even known with certainty to be a microbial disease at all.

At the very threshold of this investigation, there was the obstacle of the exciting cause of the disease being unknown, and although this obstacle still remains, it has no more blocked the way to the discovery of preventive measures than did the same obstacle in the case of small-pox so many years before.

A more formidable impediment to experimental progress was, however, the uncertainty which attends the communication of rabies by ordinary inoculation, and it is obvious that, until this difficulty had been overcome, little or no way could be made with the investigation. It was here that Pasteur exhibited that experimental sagacity which is to be found in all his work. It had been pointed out by Dr. Duboué, of Pau, that the seat of the disease in rabies is the nervous centres, and bearing this in mind, Pasteur conceived the idea of communicating the disease by taking the nerve tissue of an animal which had died of rabies and introducing it into the central nervous system, the brain, of the animal to be infected. This proved to be the key to the situation, as in this manner it was found that the virus could always be with absolute certainty conveyed from one animal to another. This ingenious mode of procedure, it should be pointed out, was not based on any pathological considerations, but was simply an adaptation of the principle which Pasteur had followed in all his researches both on fermentative and other micro-organisms, namely, to provide for each microbe that nutritive medium which was best suited to its particular requirements.

To Pasteur, then, the nervous tissue of the rabid animal appeared as a pure cultivation of rabies-virus, and in this material he now endeavoured to induce attenuation on the lines which had proved so effective in the case of fowl cholera and anthrax. Nor did these theoretical anticipations prove illusory. Thus, by changing the medium, he found the virulence could be altered; by transferring the malady to monkeys, the virulence became attenuated; by transferring it to rabbits, the virulence became intensified. But further, just as the viruses of fowl cholera and anthrax had been attenuated by the exposure of their cultures to the air, so he found also that the virus of rabies could be successfully attenuated to any desired degree by exposing the spinal cord of rabid rabbits to dry air for variable periods of time, and that if the exposure was protracted beyond 14 days, the virulence had altogether disappeared.

Thus were acquired all the materials necessary for the preventive inoculation against this terrible disease. The method of putting it in practice I cannot do better than describe in the words of M. Roux, Pasteur's able collaborateur in this, as in so many of his other masterly achievements:

"A dog which is inoculated with the spinal cord of 14 days' age, and on the following day with that of 13 days, then with that of 12, and so on up to the fresh spinal cord itself, does not take rabies, and has become refractory to it. Inoculated in the eye or in the brain with the most powerful virus, it remains well. Thus it is possible in 15 days to confer on an animal immunity against rabies. But human beings bitten by mad dogs do not usually develop rabies within a month or more of the bite. The period of incubation can, therefore, be utilised in rendering the bitten person refractory.

"Experiments made on both bitten and inoculated dogs succeeded beyond all expectation. It will be remembered how, with the assistance of M. Vulpian and M. Grancher, these experiments were extended to man. Nearly 20,000 persons have to-day undergone this antirabic treatment; the mortality amongst these treated persons has been less than 5 per 1000."

The public expression of gratitude for this great discovery, conferring such an immediate boon and serving as the foundation for even still greater material benefits in the future, took the form of a general subscription which rendered possible the foundation of the Institut Pasteur, which the great investigator had long cherished as a dream, and the realisation of which was the delight of his few remaining years, and here, under the auspices of Duclaux, Roux, Chamberland, and Metschnikoff, the sacred fire kindled by the "grand Maître" is still burning.

Long may this flame be fed within the temple where now rests in eternal sleep that hero of science whose greatest ambition was to be able in his last hour to pronounce the words, so simple in their form, so boundless in their aspiration :

"j'ai fait ce que j'ai pu."

Aug. Kekulé

KEKULÉ MEMORIAL LECTURE.*

(Delivered on December 15th, 1897.)

By Francis R. Japp, F.R.S.

The great chemist whose life and work I shall endeavour to pass in brief review before you this evening, was not one of the popular heroes of science. Whatever may have been his qualifications for playing such a part—and surely, great natural eloquence, unfailing lucidity, and a humour that enlivened the discussion of even the driest subjects, are to be thus regarded—he apparently disdained to put them to so ignoble a use as the achievement of mere popular fame. He brought an intellect of incomparable power and subtlety to bear on problems so abstruse, so remote from the everyday thoughts and interests of mankind, that the vast majority even of educated persons have never heard either of the problems, or of the man who did so much to solve them. The greater, then, is the need that we, who realise both the direct scientific value of Kekulé's work and the furthering influence which, in spite of its apparent remoteness, it has exercised indirectly on the welfare of mankind, should place on record our sense of his high deserts.

Friedrich August Kekulé—he made use of only the second of his Christian names—was born at Darmstadt on September 7th, 1829.† His father was a Hessian *Oberkriegsrath*. Even as a boy, Kekulé displayed remarkable powers; at the Gymnasium of his native town he distinguished himself in mathematics and in drawing; whilst outside the school curriculum his instincts as an observer found congenial scope in the study of the flora and butterflies of the district. After passing the leaving examination at the Gymnasium in 1847, he determined, in accordance with his father's wish, to become an architect, and for this purpose entered as *studiosus architecturæ* at the University of Giessen. Kekulé, in later life, by no means regarded the time thus spent as wasted; he always laid stress on the turn which the study of architecture had given to his thoughts; on the necessity which he ever afterwards felt of having before him, if possible, an actual picture of any problem he was dealing with. He was doubtless right. After

* Chemical Society's Memorial Lectures, No. VII.

† For the facts of Kekulé's life I am indebted partly to two obituary notices: one by Wallach (*Naturwissenschaftliche Rundschau*, 1896, **13**, 437) and the other by Königs (*Münchener Medicinische Wochenschrift*, 1896, **39**, 920); and partly to Kekulé's well known address delivered before the German Chemical Society in 1890 on the occasion of the *Kekuléfeier*.

all, he remained an architect to the last: only it was the architecture of molecules, instéad of that of buildings, with which it was his lot to concern himself.

In any case, chemists may feel thankful that Kekulé's architectural studies led him to the University, instead of into an architect's office. Liebig was then at Giessen; Kekulé attended his lectures on chemistry; and such was the fascination both of the lecturer and of the subject, that the young student resolved to abandon architecture and devote himself entirely to chemistry. His relatives insisted that he should take sufficient time to consider his decision; and he therefore returned to his native town, where he spent a semester studying ât the Polytechnic School. At the end of that time he returned to Giessen and entered the University Laboratory as a pupil of Liebig and Will. His first research, carried out under Will's guidance, was an investigation of amylsulphuric acid and its salts, published in 1850. About this time, Liebig offered Kekulé an assistantship, which, however, he declined, as he was enabled, through the generosity of a stepbrother, a merchant in London, to study for a year in Paris. Here he remained from 1851 to 1852, attended Dumas' lectures, and made the acquaintance of Wurtz, Cahours, Regnault and others. Of most influence on the formation of Kekulé's views, however, was the friendship which he formed with Gerhardt, the originator of the type theory, whose great *Traité de Chimie Organique*, then just ready for the press, he was allowed to read in manuscript. On returning to Germany, he graduated as Doctor of Philosophy at Giessen in 1852. He then obtained his first appointment, that of private assistant to Baron von Planta, at whose beautifully situated château, Reichenau, near Coire, in Switzerland, he spent a year and a half. He published, jointly with von Planta, two papers on the action of ethylic iodide on nicotine and coniine, and some elaborate analyses of Swiss mineral waters; the latter work can hardly have been very congenial to Kekulé, who, as he afterwards said, was employing the leisure and freedom from distractions which his post afforded, in elaborating the ideas which he had found in Gerhardt's unpublished manuscript. In January, 1854, he exchanged his assistantship with von Planta for a similar post with Stenhouse in London. Here he became intimate with Williamson and Odling, both of whom, but especially the former, exercised great influence on the development of his ideas. He says:

"If in Paris I had an opportunity of acquainting myself with Gerhardt's unpublished views, I had now the good fortune to enter into active friendly intercourse with Williamson and to familiarise myself with the modes of thought of this philosophical intellect.

"Originally a pupil of Liebig, I had become a pupil of Dumas, Gerhardt, and Williamson: I no longer belonged to any school."

The training which Kekulé received during these *Wanderjahre* was undoubtedly the best he could possibly have had for the task he was destined to perform. Suppose that, instead of going to Paris, he had been shortsighted enough to accept the assistantship which Liebig offered him. In that case he might have shared the fate of many promising students who have been promoted to be the assistants of their teachers; he might have gone on producing research work cut to a single pattern; he might have become a *Privatdocent* in the institution in which he was trained; and so on to the end of the chapter. Not that a man of Kekulé's originality and strength of intellect could ever have been satisfied to play the part of a mere scientific hodman; but had he been hampered by a one-sided training, it might have been much longer before he discovered where his strength as a reformer lay: in fact he might not have discovered it at all until the brief period—the too brief period—during which the great creative geniuses of science really create, was in his case past. A Kekulé trained solely in Liebig's laboratory would never have adopted the masterful attitude of the actual Kekulé towards the doctrines of the school of Berzelius; and although he might have excited the ire of some of his opponents less, organic chemistry would have moved more slowly.

Kekulé always emphasised the necessity for getting rid of preconceptions due to early training. "Free yourselves from the spirit of the school," he said; "you will then be capable of doing something of your own. Remember that it was Mephisto who gave the Scholar the advice:

> Am besten ist's auch hier, wenn Ihr nur Einen hört
> Und auf des Meisters Worte schwört."

A few months after his arrival in London Kekulé published his well-known "Note on a new Series of Organic Acids containing Sulphur" (*Annalen*, 1854, **90**, 309; *Proc. Roy. Soc.*, 1856, **7**, 37—received April 5, 1854). This paper is noteworthy as the first published work of Kekulé's which exhibits his distinctive modes of thought. Various passages contained in it clearly show that, although only briefly indicated, at least the germ of his later system, the linking of atoms in terms of their valency, was present to his mind. I will illustrate this more fully later on when I come to deal with Kekulé's theoretical views. Meanwhile, in the present merely historical connection, the interesting passage from his speech delivered before the German Chemical Society (*Ber.*, 1890, **23**, 1306) on the occasion of celebrations held in his honour, in which he describes the origin of the idea of the linking of atoms, may be quoted. The local colour should commend it to a London audience.

"During my stay in London I resided for a considerable time in Clapham Road in the neighbourhood of the Common. I frequently, however, spent my evenings with my friend Hugo Müller at Islington, at the opposite end of the giant town. We talked of many things, but oftenest of our beloved chemistry. One fine summer evening I was returning by the last omnibus, 'outside,' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie (*Träumerei*), and lo, the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain, dragging the smaller ones after them, but only at the ends of the chain. I saw what our Past Master, Kopp, my highly honoured teacher and friend, has depicted with such charm in his 'Molekularwelt'; but I saw it long before him. The cry of the conductor: 'Clapham Road,' awakened me from my dreaming; but I spent a part of the night in putting on paper at least sketches of these dream forms. This was the origin of the *Structurtheorie*."

Then he relates a similar experience of how the idea of the benzene theory occurred to him. This refers to a later period, when Kekulé was professor in Ghent, but may be quoted here in connection with the previous passage. He describes how he was at work one evening:

"I was sitting, writing at my text-book; but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures, of manifold conformation: long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

"Let us learn to dream, gentlemen," adds Kekulé, "then perhaps we shall find the truth . . . . but let us beware of publishing our dreams before they have been put to the proof by the waking understanding."

After his return from England, Kekulé went to Heidelberg, where on February 29th, 1856, he obtained the *venia legendi* in Chemistry at the University. The young *Privatdocent* fitted up a modest laboratory consisting of a room with a kitchen adjoining it. Among the few students whom he could accommodate was Adolf Baeyer, who there carried out his well-known work on the organo-arsenic compounds. Kekulé himself prepared the experiments and most of the specimens for his lectures on organic chemistry. Generally the last item of his

hard day's work was the sweeping out of the class room against next morning's lecture.

The various investigations which Kekulé published about this time, excellent as they were from an experimental point of view, were still more remarkable for the theoretical conceptions which they embodied; indeed, in the latter respect, as every chemist knows, they inaugurated a new era in organic chemistry. The two papers on the constitution of mercuric fulminate (1857 and 1858); that on the so-called conjugated compounds and the theory of polyatomic radicles (1857), which contains a complete system of multiple types and mixed types based on this theory; those on the conversion of acetic acid into glycolic acid and on chloralide (1858) and finally, the celebrated paper "On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon" (*Annalen*, 1858, **106**, 293), which contained a full statement of Kekulé's views on the linking of atoms—the foundation on which our modern system of constitutional formulæ rests—attracted the attention of chemists throughout the world, with the result that, in 1858, Kekulé, on Stas's recommendation, was called as ordinary professor of chemistry to the University of Ghent.

It might have seemed that the inspiring influence of a great chemist and teacher had thus been lost to Kekulé's fatherland. But this was not the case. Thanks to the fact that in Germany a student need not have studied at the university at which he graduates, German students are attracted to teachers rather than to institutions; in fact, in their peregrinations from one university to another, they resemble the wandering scholars of former days. Many young Germans thus made the pilgrimage to Ghent to study under Kekulé: among their number Baeyer, Glaser, Hübner, Körner, Ladenburg, Linnemann and Wichelhaus.* Later on, these disciples, as teachers in the German universities, were instrumental in disseminating Kekulé's doctrines.

The nine years which Kekulé spent in Ghent were years of great productivity. In the theoretical papers which he had up to that time published, he had laid down the lines of his future work—nay, of the future work of the organic chemists of his generation. That work would consist in experimentally verifying the innumerable predictions, and in considering the further logical consequences, of his theory.

Of the investigations belonging to this period may be mentioned: those on organic acids, their basicity and hydricity (atomicity); on the relations between succinic, malic, and tartaric acids; on the isomeric unsaturated dibasic acids—fumaric and maleic acids on the one hand, and mesaconic, citraconic and itaconic acids on the other—a marvellous piece of experimental work, in which, however, Kekulé was less for-

* Among English chemists, Dewar and G. Carey Foster studied under Kekulé in Ghent.

tunate than usual in the interpretation of his results, although, considering the complexity of the problem, this was not to be wondered at; the conversion of hydroxy-acids into bromo-acids; the electrolysis of dibasic acids; the synthesis of acids of the benzene series by the replacement of bromine in bromobenzenes by carboxyl; the elucidation of the constitution of azo- and diazo-compounds, and the transformation of diazo- into azo-compounds. The theoretical work is of course for the most part involved in the practical and cannot be discussed apart from it. One piece of theoretical work must, however, be specially mentioned. It is Kekulé's benzene theory—the crowning achievement of the doctrine of the linking of atoms. Of this, more will be said later on.

A new system of chemistry is not a proposition in Euclid, to be proved in a few words; its proofs are cumulative, and its truth or error—or to speak more accurately, its expediency or inexpediency—can be tested only by applying it to the whole body of the science. This is why so many of the great originators in our science have bent their minds to the task of writing a text-book. The text-books of Lavoisier, Berzelius, Gerhardt, Kolbe and Kekulé are cases in point.

The publication of Kekulé's *Lehrbuch der organischen Chemie* falls for the most part within the Ghent period. The first instalment appeared in 1859. The effect produced by the book was enormous. The facts of organic chemistry appeared to group themselves spontaneously under the new system. Whatever might be its ultimate fate, here was a method of exposition immeasurably superior to any that had preceded it; and as a result, every text-book of organic chemistry that has since appeared has shown more or less distinctly the influence of this remarkable work. Even Kolbe's accusation that the method owed its success to the fact that it saved chemists the trouble of thinking, may be regarded as indirect praise.

Kekulé's *Lehrbuch* was never finished. The first instalment of the third volume appeared in 1867—the year in which Kekulé left Ghent—after which further publication ceased for thirteen years. On one occasion, Kekulé received from his students an amusing reminder that they desired to see the continuation of the work. It was at a *Commers* held at Bonn in the early seventies. For the benefit of those who may be unfamiliar with German academic customs, I may explain that the *Commers* is a students' festivity in which the beer of the country plays an important part. Professors are frequently present by invitation, and just as, at the ancient *saturnalia*, the position of master and servant was reversed, so, at these mild modern *saturnalia*, there is a certain relaxation of the attitude of strict respect which the German student otherwise maintains towards his professor. Thus a professor may hear his work, or some literary or

other controversy in which he is engaged, playfully discussed in a set of occasional verses, or made the theme of a humorous dramatic interlude enacted by the students. On the occasion referred to, Kekulé, on taking his seat, found on the table in front of him what purported to be a complete, bound copy of the only partially existent third volume of his *Lehrbuch*. On closer examination it proved to be a box, in book form, containing writing materials. Kekulé enjoyed the joke, but declined to take the hint, at least for the time being. Later on, in 1880, with the collaboration of Anschütz and Schultz, he returned to the work; but with the conclusion of the third volume this second attempt also collapsed.

In 1867 Kekulé was appointed to the Professorship of Chemistry in the University of Bonn. Here he found himself at the head of a palatial laboratory, built shortly before from Hofmann's designs. During the first part of the time which he spent at Bonn his scientific activity continued, and he published various important researches, chiefly in collaboration with pupils. Among the numerous chemists who studied under Kekulé at Bonn may be mentioned: Anschütz, Bedson, Bernthsen, Carnelley, Claisen, Dittmar, Franchimont, van't Hoff, Klinger, Königs, G. Schultz, Thorpe, Wallach, and Zincke. The research work belonging to this period deals with the following subjects, amongst others: phenylmercaptan and phenylic sulphide (investigated jointly with Szuch); ethylbenzoic acid (with Thorpe); the formation of hydroxyazobenzene by the action of diazobenzene chloride on sodium phenoxide (with Hidegh); an aromatic glycolic acid —hydroxymethylbenzoic acid— (with Dittmar); the condensation products and polymeric modifications of aldehyde (with Zincke); the action of phosphorus pentachloride on sulphonic acids (with Gibertini and Barbaglia); on triphenylmethane (with Franchimont); the formation of cymene and cymyl hydrosulphide by the action of phosphorus pentasulphide on camphor (with Pott and Flesch), and of cymene by the action of iodine on oil of turpentine (with Bruylants); the constitution of the allyl compounds and of crotonic acid (with Rinne); and the well-known speculations on the constitution of isatin and isatic acid, which led, later on, to the synthesis of these compounds by Claisen and Shadwell. About the year 1876, however, Kekulé's physical powers began to show signs of failure, and for the rest of his life he practically never again enjoyed a continuance of good health. He aged prematurely and rapidly. Increasing deafness exercised a depressing effect upon him, and led him to shun the society even of his more intimate friends. Under these circumstances it is not surprising that the time which he devoted to his laboratory was greatly curtailed. There was still, however, an

occasional but unfailing incentive to research; namely, the publication, by other chemists, of results which clashed with his theoretical views. In such cases, Kekulé's suspicions of the accuracy of the observations were at once aroused; the work was carefully repeated and shown to be vitiated by some blunder; in fact, the effect of the corrected work was generally to establish Kekulé's views more securely than ever. Cases in point are the re-investigation of Tanatar's "bioxyfumaric acid" and "trioxymaleic acid," which proved to be racemic acid and mesotartaric acid respectively, published jointly with Anschütz in 1880—81; of Gruber and Barth's "carboxytartronic" (dihydroxytartaric) acid in 1883; and of Carius' "trichlorphenomalic" (trichlor-β-acetylacrylic) acid, jointly with Strecker, in 1884. The whole of this work, both experimental and theoretical, is masterly, finished in all its details, worthy of Kekulé at his best. How the supposed "carboxytartronic" acid, up to that time regarded as a pillar of Ladenburg's prism formula for benzene, was shown to be dihydroxytartaric acid and to furnish fresh evidence in favour of Kekulé's hexagon; how "trichlorphenomalic" acid, first discovered by Carius and furnished by him with a wrong formula and various self-contradictory reactions, then apparently abolished by Krafft, was finally rehabilitated, explained, and summoned as a fresh witness on behalf of the hexagon: these narratives are, to those capable of following them, of absolutely dramatic interest. Of this dramatic interest none was more conscious than Kekulé himself; he calls the story of "trichlorphenomalic" acid a "Comedy of Errors."

Kekulé's premature physical decay was, therefore, entirely unaccompanied by any corresponding failure of his mental powers. These remained fresh to the last. Even up to a few months before his death, he would, when his strength permitted, discuss with his assistants problems connected with the recent progress of chemical science.

There is no doubt that Kekulé had presumed too much on a naturally strong constitution and had undermined it by excessive study in early life. In the speech already referred to, he admits as much. I will quote the passage and also that immediately following it, which contains much excellent advice to young students:

"I have faithfully followed the counsel which my old master, Liebig, gave me when I was a young beginner. 'If you want to be a chemist,' Liebig said to me when I was working in his laboratory, 'you will have to ruin your health; no one who does not ruin his health with study will ever do anything in chemistry nowadays.' That was forty years ago. Is it still true? I faithfully followed the advice. During many years I managed to do with four and even three hours' sleep. A single night spent over my books did not count; it was only when two or three came in succession that I thought I had done

anything meritorious. At that time I had acquired such a fund of knowledge as to make my friends think that I was more trustworthy than the *Jahresbericht*.

"Those good days are long past. Of the various mental powers, imagination is the first to go; memory follows—fortunately, slowly; the longest to remain is the critical faculty, but this may still do good service, provided that it rests on the broad foundation of solid knowledge acquired by thorough industry. May I draw a moral? I would recommend my young fellow-chemists to be diligent during youth.

"One cannot explore new countries in express trains, nor will the study of even the best text-books qualify a man to become a discoverer. Whoever is content to follow well-laid promenades until he reaches some pleasant eminence frequented by tourists, may, by striking into the thickets, gather some forgotten flower; or, if cryptogams, mosses, and lichens satisfy him, may even bring home a well-filled vasculum; but anything essentially new he will not find. Whoever wishes to train himself as an investigator must study the travellers' original works; and that, too, so thoroughly that he is able to read between the lines—to divine the author's unexpressed thought. He must follow the paths of the Pathfinders; he must note every footprint, every bent twig, every fallen leaf. Then, standing at the extreme point reached by his predecessors, it will be easy for him to perceive where the foot of a further pioneer may find solid ground."

These words were spoken on the occasion of what, I believe, was Kekulé's last appearance before a public audience. The German Chemical Society had resolved to celebrate the twenty-fifth anniversary of the publication of Kekulé's benzene theory. To this end they held, in his honour, on March 11th, 1890, a festival of a magnificence perhaps unparalleled in the history of science. Chemical Societies in all parts of the world—our own, as the oldest, heading the list—united in sending delegates with addresses of congratulation. A portrait of Kekulé had been painted by H. von Angeli at the instance of the German coal tar colour manufacturers, who had adopted this means of testifying to their sense of the influence which Kekulé's theoretical views had exercised in furthering their branch of chemical industry; this portrait, which is now in the National Gallery in Berlin, was unveiled on that occasion. The President of the Society, A. W. von Hofmann, delivered one of these felicitous addresses of which I fear that the secret, so far as chemists are concerned, has died with him: in it he sketched the history of benzene from the time of its discovery as "bicarburetted hydrogen" by Faraday up to the point when Kekulé appeared, to "pluck the heart out of its mystery." Then A. von Baeyer gave a critical review of the entire field of the benzene theory, coming to the conclusion that all lines of discussion of the problem ultimately led to the solution first furnished by Kekulé. Other distinguished pupils of Kekulé's added their tribute of homage. Finally the master himself replied, in a speech which was, beyond

cavil, the culminating point of the day's proceedings, striking as these had been. It was the personal utterance of a man whose utterances had hitherto been confined mainly to the exposition of the impersonal facts and theories of his science. It was modestly autobiographical; it traced the growth and training of the speaker's powers; it afforded a glimpse into his intellectual workshop. Needless to say that it produced a profound impression. I have already given copious extracts from this speech; I only wish that time permitted me to quote the whole. It should be read by every one who desires to understand Kekulé's character and influence.

On the day preceding these celebrations, Kekulé communicated verbally * to the German Chemical Society, at the ordinary meeting of March 10th, 1890, the results of the last scientific investigation on which he was ever engaged. It was an experimental proof of the absence of a para-bond in pyridine, and was doubtless intended to have an indirect bearing on his benzene formula.

A chill which Kekulé received in April, 1896, on a journey to Cassel, told on his already weakened system. The state of his health began to occasion the gravest fears. At the same time symptoms of heart disease manifested themselves. However, his health again improved; but just when the immediate danger appeared to have passed over, he succumbed to failure of the heart's action on July 13th, 1896.

Kekulé's merits never lacked recognition. He was a member of most of the European academies and other learned societies. He was elected a Foreign Member of our own Society in 1862, and of the Royal Society in 1875. He received the Copley Medal in 1885, and the Prussian *Ordre pour le Mérite* in 1895. The present German Emperor, who, during his period of study at Bonn, was a pupil of Kekulé, revived an old title of nobility which Kekulé's family had formerly borne; and during his later years the great chemist signed himself Kekulé † von Stradonitz. Posterity, however, will probably prefer to know him by the name under which the work of his life was published.

Great as were Kekulé's powers as a thinker and an investigator, it is no exaggeration to say that he was equally distinguished as a teacher, whether in the lecture room or in the laboratory. His speech was of extraordinary ease and precision. His lectures, which were delivered, so far as my recollection goes, without notes, might have been published in the form in which they were spoken. His

* The memoir does not appear to have ever been written; at all events it was not published in the *Berichte*. A statement of the interesting results obtained, privately communicated by Kekulé himself, is, however, to be found in Anschütz's edition of Richter's *Organische Chemie*, **2**, 1896, pp. 518—520.

† The acute accent on the final *e* is dropped.

ideas were always ready at his call; thus when, in directing the work of research students, the chances of an investigation brought him upon some subject which he could not possibly have been previously considering, his exposition was as sure and as logical as in his set lectures, and save that he naturally made much freer use of colloquialisms, might, like the lectures, have been written down as it stood. The effect of his discourse was heightened by a natural play of humour, of a somewhat dry and caustic type, for the exercise of which the opinions of scientific opponents and the blunders of students equally afforded scope. He was invariably fresh and stimulating; one detected no trace of that listnessness which is so frequently the bane of speakers who are compelled to lecture year after year on the same theme to what is practically the same audience of average students. He had, moreover, the advantage of a striking personal appearance; and his face, ordinarily of a grave and reflective cast, lighted up when he spoke. His laboratory teaching, in which, during his later years at all events, he devoted himself almost exclusively to directing the work of research students, was remarkable for the way in which he endeavoured to awaken independent thought in the student; thus he did not dictate a particular course to be carried out blindly by the student, and resent any suggestion as an impertinence—a method of teaching not unknown in some laboratories where the output of research work is possibly in excess of its educational value; on the contrary, he was never better pleased than when a student was full of suggestions, which he would spend much time in patiently listening to and criticising. The one thing which he never pardoned in a student was want of interest in his work; such a student was, for the future, quietly ignored.

If one compares Kekulé's published experimental work with that of many other eminent chemists among his fellow-countrymen—with that, for example, of Liebig, or Wöhler, or Hofmann—one is struck by its much smaller volume. His ill-health affords only a partial explanation. Although no one acquainted with Kekulé's extraordinary powers of work would dream of taxing him with indolence, yet the whole of his career unmistakably showed that with him work was a means and not an end. He began by formulating certain important theoretical conceptions, and he then, for a time, exerted himself to verify them experimentally. But when he saw that his ideas had taken root, and that hundreds of willing disciples were engaged in this task of verification; when he realised that only by such general co-operation could the work be brought to a successful issue; he contented himself, for the most part, with looking on and criticising. As he said, the critical faculty was, of the various mental powers, that which survived longest. His criticism, as we have seen, frequently took the

useful form of the correction of inaccurate observations. Again, with a view to disseminating his doctrines, he began to write his text-book. But long ere the text-book was finished, it had done its work; the doctrines were almost univerally received; and the text-book remained a noble fragment.

After all, Kekulé's supreme merit lies in his contributions to theoretical chemistry. There is, here as elsewhere, a necessary division of labour, and it is irrational to complain that the intellectual gifts of a Kekulé do not include those of a Hofmann—that a Lavoisier is not also a Scheele.

It now remains to consider, somewhat more fully than has been possible in the course of the foregoing brief sketch of Kekulé's life, the main features of his theoretical work. But here a two-fold difficulty arises.

Kekulé's greatest achievements in theoretical chemistry are: the doctrine of the linking of atoms in terms of their valency, and, growing out of this, the theory of the structure of organic molecules, both in open-chain and in closed-chain compounds. Even the youngest branch of these theories—that dealing with the structure of closed-chain or cyclic compounds—has been before the world more than thirty years. Moreover, they are not recondite theories, hidden away in the depths of the science; on the contrary, they are organic chemistry itself, and our students learn them on their first introduction to the subject. In addressing an audience, therefore, of expert chemists, what new thing can be said on these well-worn themes?

The only admissible course is to take up the question of origins. Here the second difficulty presents itself.

Great theoretical conceptions are not created out of nothing. Not only is, in most cases, the substratum of experimental or observational fact on which they rest previously on record; but later historical research generally discloses the presence, scattered throughout the literature of the subject, of anticipatory germs of the theories themselves. This commonplace in the history of science finds expression in the saying that "the theory was in the air." Hence arise the innumerable claims to priority, with some of which I fear I must deal on the present occasion.

As a preliminary to the discussion of the theoretical conceptions which we owe to Kekulé, it will be necessary to consider briefly the state of organic chemistry at the time when he came upon the scene.

The dualistic electro-chemical theory elaborated by Berzelius, which for many years had dominated the entire field of chemistry, had, so far as organic chemistry was concerned, fallen before the attacks of

Dumas, Laurent, and the other supporters of the doctrine of substitution. In 1842, Melsens showed that trichloracetic acid could be re-converted into acetic acid; and Berzelius, compelled at length to admit that the two compounds belonged to the same class, made a noteworthy concession to the doctrine of substitution. Unable to accept without qualification the view that elements so widely separated in the electro-chemical scale as hydrogen and chlorine could mutually replace one another in compounds without materially changing the properties of the latter, he devised the doctrine of conjugated compounds, and limited the operation of this process of substitution to the conjuncts. Thus acetic acid and trichloracetic acid were conjugated oxalic acids in which the respective conjuncts were C_2H_3 and C_2Cl_3;

Acetic acid	$C_2H_3 + C_2O_3 + HO$
Trichloracetic acid	$C_2Cl_3 + C_2O_3 + HO$

According to Berzelius, the replacement of hydrogen by chlorine, as long as it was confined to the conjunct, did not materially change the properties of the compound.

This limitation of the action of substitution to the conjuncts, and indeed the entire theory of conjugated compounds, has generally been looked upon as an unconscious subterfuge, adopted by Berzelius to cover his retreat. I think, however, that, regarded even from the standpoint of our modern electro-chemical theories, the limitation appears a perfectly legitimate one. The error in Berzelius' original system was an error of excess: it had arisen from applying conceptions drawn from the behaviour of electrolytes, or ionisable compounds, to non-electrolytes, or non-ionisable compounds. In making the limitation just referred to, Berzelius merely withdrew the previous undue extension of his system, whilst retaining the portions which still held good. It is precisely when a halogen atom replaces hydrogen of the conjunct—that is, of the hydrocarbon radicle of a compound—that it is not ionisable; and it is only when the substituents are non-ionisable that the Dumas-Laurent statement of the law of substitution is valid. I mention this, because it appears to me that, in this matter, Berzelius hardly received justice from his opponents. Kekulé, for example, ridiculing Berzelius' change of front, says (*Lehrbuch*, 1, 74—75): "That which had been absurd as long as it was regarded without any hypothesis, became 'surprisingly clear and simple' when seen through the medium of the hypothesis of the conjuncts . . . . In his joy over the conjuncts, he [Berzelius] had forgotten that his object was to combat the theory of substitution."

The chief point, however, is that Berzelius and his school were thus compelled to abandon their doctrine of the unchangeable nature of compound radicles.

Kolbe, the great continuator of Berzelius' system, adopted and extended this doctrine of the conjuncts. At the same time he introduced the conception of more complex radicles (*nähere Radicale*) which were built up from simpler radicles (*entferntere Radicale*). Thus, according to Kolbe, acetic acid contains a conjugated radicle, $C_2H_3\hat{}C_2$ (called by Kolbe "acetyl") consisting of carbon conjugated with methyl; this unites with oxygen to form $C_2H_3\hat{}C_2O_3$, acetoxyl; and the latter in turn combines with water to form acetic acid, $C_2H_3\hat{}C_2O_3.HO$. This view of the constitution of acetic acid is, as will be seen, not far removed from that now held; it clearly indicates that one half of the carbon in the molecule is present as methyl, whilst the other half serves to satisfy the affinity of oxygen.

Kolbe's extraordinary power of expressing chemical reactions in terms of chemical constitution was unfortunately coupled with an almost complete inability to realise the force of arguments drawn from physical laws. One result was that until 1870 he continued to use Gmelin's equivalents instead of our present atomic weights. There can be little doubt that this both hampered his efficiency as an investigator and prevented his theoretical views from being received at their full value. Kolbe, however, afterwards contended that his mistaken adherence to the old equivalents had facilitated his discovery of the constitution of acids, aldehydes, and ketones, and his prognosis of secondary and tertiary alcohols.

Thanks mainly to the conceptions of chemical structure which we owe to Kekulé, we can, looking back on the disputes which raged round the radicle theory, perceive where truth lay, and where error; nay, we can often see that, of two competing rational formulæ, both were right, each affording a partial glimpse of a truth which afterwards found its fuller expression in the structural formula of the compound. But Kekulé's predecessors were not in this position, and it is not surprising that the manifold hypotheses, and the contradictions, real or apparent, of the radicle theory led many to regard the problem of the constitution of chemical compounds, at least in the sense in which the supporters of this theory understood it, as insoluble.

Gerhardt was one of those who held this view, and in his earlier exposition of his "unitary system" (1848) he employed empirical formulæ only. His chief efforts were at that time directed to representing the various chemical compounds by comparable quantities—their molecular weights—and for this purpose he selected as his unit the molecular weight of water, the formula of which he wrote H_2O. He employed our present atomic weights for carbon, oxygen, sulphur and their analogues; but somewhat misleadingly called these atomic weights "equivalents."

The difficulty of dealing with organic compounds by means of empirical formulæ alone, led Gerhardt to extend his original system, and to introduce into the formulæ certain atomic groups which he termed "residues." When two compounds interact, eliminating jointly the elements of water or of some simple inorganic compound, the two residues of the original compounds combine. Thus, in the formation of nitrobenzene from benzene and nitric acid, water is eliminated, and the "benzene residue," C_6H_5, unites with the "nitric acid residue," NO_2. The so-called residues were thus in many cases identical with the old radicles (leaving out of account the fact that Gerhardt used the new atomic weights), and the system was an attempt to secure the benefits of the radicle theory whilst avoiding its more or less hypothetical basis. The way was thus paved for the union of the radicle theory with Dumas' type theory, the outcome of which union was Gerhardt's type theory.

As regards the latter theory, the idea of the ammonia type was furnished by the researches of Wurtz and Hofmann (1849–50) on the substituted ammonias, in which 1, or 2, or 3 hydrogen atoms of the original ammonia molecule were replaced by alcohol radicles. Williamson (1850) showed that alcohol and ether might in like manner be derived from 1 mol. of water by the replacement of either 1 or 2 hydrogen atoms by such radicles; and in the following year (1851) he adopted a similar view in the case of the acids; thus, he regarded acetic acid as 1 mol. of water in which a hydrogen atom is replaced by acetyl, C_2H_3O. Shortly afterwards (1852), Gerhardt, applying to the monobasic acids a method analogous to that by which Williamson had effected the synthesis of ether, obtained acetic anhydride and its analogues, which were thus shown to stand in the same relation to the monobasic acids as the ethers to the alcohols.

When once it had been recognised that organic compounds might be derived by substitution (double decomposition) from simple inorganic compounds like water and ammonia, and might therefore be formulated on the *type* or pattern of these, the process of finding other simple inorganic compounds which should serve a similar purpose and so complete the type theory, was a tolerably obvious one. Gerhardt selected, as his four types, hydrogen (free hydrogen was, according to the Laurent-Gerhardt view, a compound, H_2), hydrochloric acid, water, and ammonia. The typical formulæ were not intended to indicate the constitution of the compounds as the term was understood by the adherents of the radicle theory. If two compounds belonged to the same type it meant merely that they had in common certain functions and certain modes of formation and decomposition.

The idea of valency, both of elements and of compound radicles, had already been propounded. In his well-known paper "On the

Constitution of Salts" (1851 *), Williamson points out that certain compound radicles, such as C_2H_3O and NO_2, can replace 1 atom of hydrogen in 1 mol. of water, giving rise to monobasic acids; whilst others, like CO, C_2O_2, and SO_2, can replace 2 atoms of hydrogen in 2 mols. of water, yielding dibasic acids. That the linking function of these dyad groups was clearly present to his mind is shown by the following passage (this Journal, 1852, **4**, 353) in which, speaking of Wurtz's decomposition of ethylic isocyanate by potassium hydroxide, he says: "One atom of carbonic oxide is here equivalent to 2 atoms of hydrogen, and by replacing them, *holds together* the 2 atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound, $\overset{(CO)}{K_2}O_2$, carbonate of potash." This important passage contains the earliest statement of the fact that a double type (here the double water type) is possible only when the compound contains a dyad radicle. Later on, in 1854, Williamson (*Proc. Roy. Soc.*, **7**, 11) showed that, by the action of phosphorus pentachloride on sulphuric acid, sulphuryl chlorhydrate and sulphuryl dichloride could successively be obtained, thus proving sulphuric acid to have the formula $SO_2(OH)_2$ which he had previously assigned to it, but which had been called in question by Gerhardt. In the same year he prepared, jointly with his pupil Kay (*loc. cit.*, p. 135), the tribasic formic ether (ethylic orthoformate), $CH(OC_2H_5)_3$ by the action of chloroform on sodium ethoxide, and pointed out that it was "a body in which the hydrogen of three atoms of alcohol is replaced by the tribasic radical of chloroform." About the same time, Odling (this Journal, 1855, **7**, 1) extended Williamson's views on the constitution of salts and assumed the presence of a triad radicle PO‴ in the acids of phosphorus: thus orthophosphoric acid was formulated on the triple water type as $\left.\begin{matrix}PO''' \\ 3H'\end{matrix}\right\}O_3$. And just as Williamson had shown that the dyad group SO_2 could unite two water residues to form sulphuric acid—a double water type—so Odling employed this same group to unite together a water residue and a sulphuretted hydrogen residue to form thiosulphuric acid—a mixed type; he formulated sodium thiosulphate $\left.\begin{matrix}SO_2'' \\ 2Na'\end{matrix}\right\}O''+S''$. He thus laid down the conditions under which a mixed type might exist: namely, when the molecule contains a polyad radicle capable of holding together the various residues.† In the same

* First published in the *Chemical Gazette* for 1851; afterwards reprinted in full in the *Journ. Chem. Soc.*, 1852, **4**, 350.

† Ladenburg (*Entwicklungsgeschichte der Chemie*, 2nd ed., p. 232) credits Gerhardt and Chiozza with having, in 1854, derived succinamic acid from the mixed type NH_3+H_2O in which the two residues were united by the dyad radicle succinyl. In that case these chemists would have anticipated Odling in showing how mixed types

year. Berthelot showed that glycerol formed ethereal salts containing 1, 2 and 3 radicles of a monobasic acid, a result which Wurtz correctly interpreted as proving that glycerol was a trihydric alcohol $\left.\begin{matrix}C_3H_5''' \\ H_3\end{matrix}\right\}O_3$, formulating it on the triple water type. From this Wurtz was led to foresee the existence of a class of dihydric alcohols, the first member of which, glycol, $\left.\begin{matrix}C_2H_4'' \\ H_2\end{matrix}\right\}O_2$, he prepared in the following year (1856). Chemists were thus beginning to familiarise themselves with the idea of polyvalent compound radicles of different hydrogen-replacing power.

In the memoir just quoted, Odling employs his well-known valency marks to indicate the valency not only of compound radicles, but also of elements. The conception of a valency of the elementary atoms was introduced into chemistry by E. Frankland in 1852. As Frankland's claims in this respect have been called in question by at least one member of the Kekulé school and were never openly acknowledged by Kekulé himself, I will quote the original passage more fully than would otherwise have been necessary. It occurs at the end of a paper "On a New Series of Organic Bodies containing Metals" (*Phil. Trans.*, 1852, 417). Frankland, who up to that time had been a follower of Kolbe, now criticises unfavourably Kolbe's doctrine of conjugated compounds. After referring to Kolbe's view that cacodyl is "arsenic conjugated with two atoms of methyl, $(C_2H_3)_2As$" (Frankland uses Gmelin's equivalents in this paper), and pointing out that the various organo-metallic compounds obviously belong to the same class as cacodyl, he proceeds (*loc. cit.*, p. 439):

"It is generally admitted that when a body becomes conjugated, its essential chemical character is not altered by the presence of the conjunct: thus for instance, the series of acids $C_nH_nO_4$, formed by the conjunction of the

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should be formulated. What they really say, however, is: "Succinamic acid represents the hydrate of an ammonium in which 2 atoms of hydrogen are replaced by their equivalent of succinyl:

$$\left.\begin{matrix}NH_4 \\ H\end{matrix}\right\}O \qquad \left.\begin{matrix}N(C_2H_5)_4 \\ H\end{matrix}\right\}O \qquad \left.\begin{matrix}N(C_4H_4O_2)H_2 \\ H\end{matrix}\right\}O"$$

(*Compt. rend.*, 1854, **38**, 458), which is a very different matter. Ammonium hydrate is here formulated on the water type, and succinyl replaces two atoms of hydrogen in ammonium: it does not link two residues together. Bearing in mind that, in Part 4, vol. 4 of the *Traité*, Gerhardt formulates the ammonium compounds with pentad nitrogen, it would seem that Ladenburg has read into Gerhardt and Chiozza's formulæ a meaning that was not present to the minds of the authors.

Gerhardt had not grasped Williamson's principle that polyvalent radicles are necessary to link together the residues in multiple types, and in Part 4, vol. 4 of the *Traité* he frequently writes formulæ that are quite at variance with it: thus $\left.\begin{matrix}C_3H_5O \\ H_3\end{matrix}\right\}O_2$ for glycerol; $\left.\begin{matrix}(C_7H_5)_3 \\ H_3\end{matrix}\right\}N_2$ for hydrobenzamide.

radicals $C_nH_{(n+1)}$ with oxalic acid, have the same neutralising power as the original oxalic acid; and, therefore, if we assume the organo-metallic bodies above mentioned to be metals conjugated with various hydrocarbons, we might reasonably expect, that the chemical relations of the metal to oxygen, chlorine, sulphur, &c., would remain unchanged; a glance at the formulæ of these compounds will, however, suffice to show us that this is far from being the case: it is true that cacodyl forms protoxide of cacodyl and cacodylic acid corresponding to a somewhat hypothetical protoxide of arsenic, which, if it exist, does not possess any well-defined basic character, and the other to arsenious acid; but no known compound corresponding to arsenic acid can be formed, and yet it cannot be urged that cacodylic acid is decomposed by the powerful reagents requisite to procure further oxidation, for concentrated nitric acid may be distilled from cacodylic acid without decomposition or oxidation in the slightest degree; the same anomaly presents itself even more strikingly in the case of stanethylium, which, if we are to regard it as a conjugate radical, ought to combine with oxygen in two proportions at least, to form compounds corresponding to protoxide and peroxide of tin; now stanethylium rapidly oxidises when exposed to the air, and is converted into pure protoxide; but this compound exhibits none of that powerful tendency to combine with an additional equivalent of oxygen, which is so characteristic of protoxide of tin; nay, it may even be boiled with dilute nitric acid without evincing any signs of oxidation: I have been quite unable to form any higher oxide than that described; it is only when the group is entirely broken up and the ethyl separated, that the tin can be induced to unite with another equivalent of oxygen. Stibethyl also refuses to unite with more or less than two equivalents of oxygen, sulphur, iodine, &c., and thus forms compounds which are not represented amongst the combinations of the simple metal antimony.

"When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony, and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, SbH_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, &c.; and in the five-atom group NO_5, NH_4O, NH_4I, PO_5, PH_4I, &c. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, *no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms.* It was probably a glimpse of the operation of this law among the more complex organic groups, which led Laurent and Dumas to the enunciation of the theory of types; and had not those distinguished chemists extended their views beyond the point to which they were well supported by then existing facts—had they not assumed that the properties of an organic compound are dependent upon the position, and not upon the nature of its single atoms, that theory would undoubtedly have contributed to the development of the science to a still greater extent than it has already done; such an assumption could only have

been made at a time when the data upon which it was founded were few and imperfect, and, as the study of the phenomena of substitution progressed, it gradually became untenable, and the fundamental principles of the electro-chemical theory again assumed their sway. The formation and examination of the organo-metallic bodies promise to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable; for, whilst it is evident that certain types of series of compounds exist, it is equally clear that the nature of the body derived from the original type is essentially dependent upon the electro-chemical character of its single atoms, and not merely upon the relative position of those atoms. . . .

"Taking this view of the so-called conjugate organic radicals, and regarding the oxygen, sulphur, or chlorine compounds of each metal as the true molecular type of the organo-metallic bodies derived from it by the substitution of an organic group for oxygen, sulphur, &c., the anomalies above mentioned entirely disappear, and we have the following inorganic types and organo-metallic derivatives:—

Inorganic types.	Organo-metallic derivatives.	
$As\left\{\begin{matrix}S\\S\end{matrix}\right\}$	$As\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}$	Cacodyl.
$As\left\{\begin{matrix}O\\O\\O\end{matrix}\right\}$	$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\end{matrix}\right\}$	Oxide of Cacodyl.
$As\left\{\begin{matrix}O\\O\\O\\O\\O\end{matrix}\right\}$	$As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right\}$	Cacodylic acid.
$Zn\ O$	$Zn\ (C_2H_3)$	Zincmethylium.
$Zn\left\{\begin{matrix}O\\O_x\end{matrix}\right\}$	$Zn\left\{\begin{matrix}C_2H_3\\O_x\end{matrix}\right\}$	Oxide of Zincmethylium.
$Sb\left\{\begin{matrix}O\\O\\O\end{matrix}\right\}$	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}$	Stibethine.
$Sb\left\{\begin{matrix}O\\O\\O\\O\\O\end{matrix}\right\}$	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\O\\O\end{matrix}\right\}$	Binoxide of Stibethine.
$Sb\left\{\begin{matrix}O\\O\\O\\O\\O\end{matrix}\right\}$	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\O\end{matrix}\right\}$	Oxide of Stibethylium.
$Sn\ O$	$Sn\ (C_4H_5)$	Stanethylium.
$Sn\left\{\begin{matrix}O\\O\end{matrix}\right\}$	$Sn\left\{\begin{matrix}C_4H_5\\O\end{matrix}\right\}$	Oxide of Stanethylium
$Hg\left\{\begin{matrix}I\\I\end{matrix}\right\}$	$Hg\left\{\begin{matrix}C_2H_3\\I\end{matrix}\right\}$	Iodide of Hydrargyro-methylium."

The foregoing extract from Frankland's paper contains a complete statement, in terms of Gmelin's equivalents, of the valency of the various elementary substances employed as "grouping elements" (to make use of a term introduced later by Frankland) in the formulæ given. In the case of the perissads—nitrogen, phosphorus, arsenic, and antimony—the valencies are 3 and 5, being thus identical with those now assigned to these elements. Arsenic appears in cacodyl as a dyad —a pseudo-dyad, as Frankland would have called it later. In the case of the artiads, zinc and tin, the atomic weight is twice the equivalent; hence the valency given by Frankland must be doubled. Mercury has been taken with the atomic weight 200, and its valency is correctly given.

Another important point is, that Frankland rejects the conception of conjugated compounds and writes typical formulæ explicitly based on the valency of the elements.

One result of Frankland's employing Gmelin's equivalents was that his statement of the law of valency did not impress the adherents of the type theory so much as it might otherwise have done. Kekulé, who in the introduction to his *Lehrbuch* fully acknowledges his obligations to "Williamson and Odling, Hofmann and Wurtz," does not mention Frankland; and a similar omission occurs in Würtz's *Atomic Theory*. Kekulé, as already mentioned, never expressed himself, at all events in his published writings, on the subject of Frankland's claims; but, if we have not Kekulé's "official" opinion on the subject, we have an opinion, put forward in a paper published by Baeyer in 1858, when the latter was a student in Kekulé's laboratory, which must, I think, be regarded as "semi-official." Baeyer gives a list of compounds formed by the union of monads alone (methyl and chlorine) with the elements of the nitrogen group, in which the latter exhibit either triadic or pentadic character—belonging, as Baeyer expresses it, either to the ammonia type, or to the ammonium chloride type—and adds (*Annalen*, 1858, **105**, 274):—

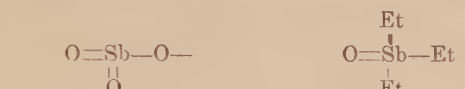
"I would here remind the reader of the series of compounds which Frankland gave in his investigations on zinc-ethyl, in which he drew a parallel between the compounds of the metals with oxygen and those with the alcohol radicles, whilst the latter are analogous to hydrogen and not to oxygen. The view which is thus gained is purely superficial; it vanishes immediately when the proper atomic weight of oxygen is adopted, and the formulæ which contain an odd number of atoms of that element are doubled."

With regard to the foregoing passage, I think we may lay it down as a safe general principle, to be adopted in dealing with this interesting period of chemical history, that a discovery, made by an adherent of the radicle theory and correctly formulated by him in terms of the

old equivalents, does not become the property of the first adherent of the type theory who happens to translate it into the new atomic weights.

Baeyer's criticism has been replied to by Frankland in the introduction to the series of papers on organo-metallic compounds reprinted in his *Experimental Researches* (p. 153). As some chemists may not have seen the passage, I will quote it :—

"Exception has been taken, I think somewhat unfairly [here Baeyer's criticism is given as a footnote], to the analogies upon which, in the following papers, I have founded the doctrine of atomicity. It has been stated, for instance, that there is no real analogy between antimonic anhydride and antimonic triethoxide, if the dyadic atom of oxygen be used in the formula of the first—that the real analogy is between antimonic chloride and antimonic triethoxide, &c. But even in the light of our most recent conceptions of the constitution of chemical compounds, the analogies which I pointed out are strictly correct ; for in antimonic anhydride each atom of antimony has five bonds satisfied by oxygen, whilst in the organo-metallic analogue, antimonic triethoxide, the oxygen of three of these bonds has been replaced by ethyl :



Antimonic anhydride. Antimonic triethoxide.

"At the time when the second paper of this chapter was written, I employed, in common with nearly all chemists, what is known as the small atom of oxygen ($O=8$). With this atomic weight oxygen was monadic ; and as it formed the only pentadic inorganic compound of arsenic, it lent itself, on the whole, better to the expression of my analogies than either chlorine, bromine, or iodine ; but (and it is on this ground that I complain of the unfairness of my critic) I distinctly stated * that I regarded 'the oxygen, sulphur, or *chlorine* compounds of each metal as the true molecular types of the organo-metallic bodies derived from them by the substitution of an organic group for oxygen, sulphur, &c.,' and I actually used, in the table of analogous compounds, HgI_2 as the type of HgMeI."

If Kekulé did not express himself regarding Frankland's claims, he went further than this, for he claimed to have been himself the first propounder of the doctrine of the valency or, as he termed it, the atomicity, of the elements. In a note "On the Atomicity of the Elements" (*Compt. rend.*, 1864, **58**, 510), published in reply to views put forward by Naquet and others, he says : "I consider that it is all the more my duty to intervene in this discussion, seeing that, if I am not mistaken, it was I who first introduced into chemistry the conception of the atomicity of the elements." (It should be mentioned that the first occasion on which Kekulé refers to valency is in his paper on thiacetic acid, published in 1854, two years later than Frankland's

* See the extract from Frankland's paper already given.

paper.) He then proceeds to combat the doctrine of varying valency: the equivalent of an element may vary; but its valency is as invariable as its atomic weight. Neither is valency to be regarded as identical with maximum capacity for saturation: thus, in reply to Naquet, who regarded iodine as triadic and the elements of the sulphur group, including oxygen, as tetradic, he points out that if iodine is a triad in ICl_3, tellurium must be dodecadic in TeI_4—a supposed *reductio ad absurdum* which Kekulé's opponents might justly regard as a travesty of their views. He then defines the conditions which, he considers, alone render the determination of the valency of an element possible: the element in question must be combined solely with monads, and the resulting compound must be volatile without decomposition. Such a compound he regards as *atomic*. Two or more atomic molecules may unite to form a *molecular* compound; such a compound may be distinguished by the fact that, when volatilised, it dissociates; it is not available for the purpose of determining the valency of the elements which it contains. Thus ICl, PCl_3, and NH_3, are atomic compounds, and their formulæ show iodine to be monadic, and phosphorus and nitrogen to be triadic. Iodine trichloride, phosphorus pentachloride, and ammonium chloride are represented as molecular compounds, ICl,Cl_2; PCl_3,Cl_2; NH_3,HCl. (At that time the existence of phosphorus pentafluoride, a compound of pentadic phosphorus gaseous at ordinary temperatures, and the fact that dry ammonium chloride may be vaporised without dissociation, were, of course, unknown.) Again, referring to his doctrine of fixed valency, he speaks (*loc. cit.*, p. 512) of "the reasoning which has made me remain faithful to my original manner of viewing the subject, and which, I venture to hope, will end by carrying the day against the modifications which have been proposed since." Surely, Frankland's doctrine of varying valency was earlier in the field!

Of all the doctrines which we owe to Kekulé that of fixed valency is probably the one which has met with least acceptance, even among chemists of his own school. At the present day it is, so far as I am aware, without supporters. Yet Kekulé held it to the last.

Whilst we must thus admit that it was with Frankland and not with Kekulé that the idea of the valency of elementary substances originated, we are in a position, I think, to explain how it was that Kekulé came to ignore Frankland's work and to claim the theory for himself. To Kekulé, varying valency and, moreover, varying valency referred to equivalents instead of to atoms, was not valency at all, as he understood it. We must bear in mind the attitude of the two opposed schools in questions of chemical theory: how each seemed to labour under an absolute inability to place itself in the mental position of the other. I have no doubt that Kekulé paid very little atten-

tion to Frankland's theoretical views ; that he evolved the doctrine of valency in part independently and in part from the indications which he found in the writings of Williamson, Odling, and Wurtz ; and that afterwards, perceiving that Frankland had put forward similar ideas, he came to the conclusion that they had not been deduced by a legitimate process and were not correctly stated.

These considerations, which may have appeared important at the time, need not weigh with us at the present day. The battle between the radicle theory and the type theory is long past. The victory was not entirely with either, for the theory of chemical structure, based on the doctrine of valency, absorbed and assimilated both. Frankland correctly perceived that the views which he was advocating promised "to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been considered irreconcilable." But the theory of chemical structure which effected this fusion is imperishably associated with the name of Kekulé, and, therefore, if he did not originate the doctrine of valency, no other chemist used it to so good purpose. Frankland, speaking of valency, says (*Experimental Researches*, p. 154) : "I do not forget how much, in its present developments, this law owes to the labours of other chemists, especially to those of Kekulé and Cannizzaro. Indeed, until the latter had placed the atomic weights of the metallic elements on their present consistent basis, the satisfactory development of the doctrine was impossible."

In his later years, Kekulé looked back upon those troublous times with a more tolerant eye. I again quote from his Berlin address :

"No science has developed so steadily as chemistry, although during one period of its development which fell partly within my own experience, the very opposite seemed for a time to be the case. Fifty years ago, the stream of chemical progress had divided into two branches. The one flowed, chiefly on French soil, through luxuriant flower-decked plains ; and those who followed it, with Laurent and Dumas at their head, could reap, during the whole voyage, almost without effort, an abundant harvest. The other followed the course indicated by an old and approved guide-post set up by the great Swedish chemist, Berzelius ; it led for the most part through broken boulders, and only later on did it again reach fertile country. At length, as the two branches had again approached much nearer to one another, they were separated by a thick growth of misunderstandings, so that those who were sailing along on the one side neither saw those on the other, nor understood their speech. Suddenly a loud shout of triumph resounded from the host of the adherents of the type theory. The others had arrived—Frankland at their head. Both sides saw that they had been striving towards the same goal, although by different routes. They exchanged experiences ; each side profited by the conquests of the other ; and with united forces they sailed onward on the reunited stream. One or two held themselves apart and sulked ; they thought

that they alone had held the true course—the right fair-way—but they followed the stream.

"Our present opinions do not, as has frequently been asserted, stand on the ruins of earlier theories. None of the earlier theories has been recognised by later generations as entirely false; all, when stripped of certain ill-proportioned, meaningless excrescences, could be utilised in the later structure, and form with it one harmonious whole.

"Here and there a seed may have lain in the ground without germinating; but everything that grew came from seed that had been previously sown. My views also have grown out of those of my predecessors and are based on them. There is no such thing as absolute novelty in the matter."

I have allowed the protagonists to speak for themselves, and so great is their agreement, at least in their later utterances, that it seems almost superfluous to call in the aid of an umpire. For the sake of completeness, however, I venture to do so. Ladenburg, although a pupil of Kekulé and thoroughly imbued with his master's teaching, has displayed, in his well-known historical treatise, a most praiseworthy spirit of impartiality in dealing with the various questions at issue between the adherents of the radicle and the type theories. Referring to Frankland's enunciation of the doctrine of valency already quoted, he says (*Entwicklungsgeschichte der Chemie*, 2nd ed., p. 251):—

"With this memoir of Frankland's the first step was taken towards a reconciliation of the hitherto opposed schools—the means was furnished for a mutual understanding. This means was destined to lead to a fusion of the different opinions, and out of the fusion the theory of valency developed. It was a gain for the adherents of the type theory to have secured Frankland's adhesion to their principles; for he brought with him ideas foreign to their modes of thought and capable of being turned to excellent account. I will not assert that the former school could not have taken the final great step—the differentiation of the atoms in terms of their valency—independently; but, having regard to the course which the development actually followed, the influence of Kolbe, and especially of Frankland, on the representatives of the Gerhardt-Williamson school (Wurtz, Kekulé and Odling) can hardly be mistaken. The efforts of both schools were necessary to impart to formulæ the significance which they afterwards acquired."

I have treated this question of the authorship of the doctrine of valency at considerable length; but the subject seemed to me by its importance to justify this, especially in the present connection, seeing that the whole of Kekulé's work is based on this doctrine.

We must now pass on to consider the use which Kekulé made of the ideas which he found scattered throughout the writings of his predecessors; how he added to them; and how he welded the whole

into the coherent system which forms our present theory of the structure of organic compounds.

Kekulé's first published work of theoretical importance was, as has already been mentioned, his "Note on a New Series of Organic Acids containing Sulphur" (*Annalen*, 1854, 90, 309). He treats various organic compounds of the water type, such as acetic acid and acetic anhydride, with the sulphides of phosphorus, and in this way replaces the typical oxygen by sulphur. He compares the action with that of the chlorides of phosphorus and significantly remarks: "One sees, indeed, that the decomposition is essentially the same; only, when the chlorides of phosphorus are employed, the product breaks up into chloride of othyl [acetylic chloride] and hydrochloric acid, or into two atoms of chloride of othyl, as the case may be; whereas, on employing the sulphur compounds of phosphorus, both groups remain united, *because the quantity of sulphur equivalent to* 2 *atoms of chlorine is not divisible.*" Elsewhere, in the same paper, he refers this difference to "the *dibasic* nature of sulphur." He then proceeds to defend Gerhardt's new atomic weights, and declares the formulæ written with these to be a better expression of the facts than the prevailing formulæ. He says: "It is not merely a difference in the mode of writing, it is an actual fact, that 1 atom of water contains 2 atoms of hydrogen and only 1 atom of oxygen; and that the quantity of chlorine equivalent to *one* atom of oxygen is divisible by 2, whereas sulphur, like oxygen itself is *dibasic*, so that 1 atom is equivalent to 2 atoms of chlorine."

We thus see that the theory of the linking of atoms and groups by means of polyad radicles was already present to Kekulé's mind. Moreover, as was always the case with him, the thought is expressed with such precision and emphasis, as to render it impossible for even the least attentive reader to overlook his meaning.*

After this apparently unconditional acceptance of Gerhardt's atomic weights, it may surprise us to find Kekulé returning in his next published work to the use of Gmelin's equivalents. The same concession to the prevailing usage was, however, made by other members of the Gerhardt-Williamson school whenever they were merely stating experimental results, or explaining theories for the understanding of which the new atomic weights were not required. Later on, in adopting the new atomic weights, the adherents of this school used, as is well known, crossed symbols for the artiads, thus: $\overline{C} = 12$, $\overline{O} = 16$, as proposed by Williamson, partly in order to indicate

* Kolbe's well-known hostile criticisms on Kekulé's literary style deal almost exclusively with verbal points: they seldom touch the meaning, which indeed Kolbe's own preconceptions prevented him from grasping. This, it need hardly be said, is written in no spirit of detraction of Kolbe's own work and influence.

that the atom was in these cases equal to twice the equivalent, and partly to avoid confusion with the uncrossed symbols which were employed by the opposed school to denote the old equivalents. Kekulé continued to use these crossed symbols until 1867. How liable to misinterpretation these concessions to the prejudices of opponents were, and how little gratitude they evoked, may be seen from the accusations which Kolbe (*J. pr. Chem.*, 1881, [ii], **24**, 398) brings against Kekulé: firstly, of having until 1857 held the view that the old equivalents were identical with the true atomic weights, whereas we have seen that as early as 1854 Kekulé had perfectly clear views to the contrary, although he for some time continued to use the equivalent formulæ for purposes of exposition; and secondly, of afterwards, "until 1867, attributing the atomic weight 16, not, strictly speaking, to the single oxygen atom, but to the double oxygen atom O." Kolbe goes on to state that he himself adopted the new atomic weights in 1870, and draws the comforting conclusion that Kekulé anticipated him in this course by only three years!

The first of these papers in which Kekulé reverts to the use of the old equivalents is entitled "On the Constitution of Fulminic Acid" (*Annalen*, 1857, **101**, 200), and was followed a year later by a second paper on the same subject. The experimental work was difficult and dangerous. The conclusion at which Kekulé arrived, namely, that fulminic acid is nitroacetonitrile is no longer held by chemists; but the work is of great interest. Perhaps the most important point in the paper is a tabular arrangement of compounds of the marsh gas type: the earliest enunciation of the tetravalency of carbon. After ascribing to mercuric fulminate the formula $C_2(NO_4)(C_2N)Hg_2$, Kekulé adds (*loc. cit.*, p. 204):

"This formula shows at the first glance that mercuric fulminate exhibits in its composition the closest analogy with a large number of known compounds, to which, for example, chloroform, $C_2\,H\,Cl\,Cl\,Cl$, belongs. We might regard it as nitrated chloroform in which the chlorine is replaced partly by cyanogen and partly by mercury.

"The following compounds may be referred to the same type:

"C_2	H	H	H	H	Marsh gas.
C_2	H	H	H	Cl	Methylic chloride, &c.
C_2	H	Cl	Cl	Cl	Chloroform, &c.
C_2	(NO_4)	Cl	Cl	Cl	Chloropicrin.
C_2	(NO_4)	(NO_4)	Cl	Cl	Marignac's oil.
C_2	(NO_4)	Br	Br	Br	Bromopicrin.
C_2	H	H	H	(C_2N)	Acetonitrile.
C_2	Cl	Cl	Cl	(C_2N)	Trichloracetonitrile.
C_2	(NO_4)	Hg	Hg	(C_2N)	Mercuric fulminate.
C_2	(NO_4)	H	H	(C_2N)	Hypothetical fulminic acid.

". . . In assigning these compounds to the same type, I do not use the word in the sense which it bears in Gerhardt's unitary theory, but in that in which it was first employed by Dumas on the occasion of his fruitful investigations on the subject of types. I wish essentially to indicate the relations in which the said compounds stand to one another; that the one, under the influence of appropriate agents, can be produced from, or transformed into, the other."

I have quoted this passage somewhat fully because Kolbe (*J. pr. Chem.*, 1881, [ii], **23**, 374, footnote) has denied that Kekulé here refers mercuric fulminate to the marsh gas type and, indeed, that the passage affords any justification for ascribing to Kekulé the enunciation of the marsh gas type and of the tetravalency of carbon. He bases this denial on Kekulé's statement that he uses the word "type" in Dumas' sense ("mechanical type") and not in Gerhardt's sense ("chemical type"). Why this statement should deprive Kekulé of all right to the theory which he so clearly expresses in his formulæ, Kolbe does not explain, unless, indeed, the explanation is to be found in a reference which he makes a little further on (*loc. cit.*, p. 375) to Kekulé's paper "On the So-called Conjugated Compounds," and in which, speaking of Kekulé's direct statement that carbon can be shown to be "tetrabasic or tetratomic," he says: "He nevertheless feels so uncertain of his ground, that he still hesitates to add the type 'marsh gas' to Gerhardt's three types."

The meaning of Kekulé's remark about types, which Kolbe has, it seems to me, entirely mistaken, is perfectly clear if we view it by the light of the various statements on the subject of types to be found in Kekulé's writings. Kekulé's types (compare *Annalen*, 1857, **104**, 132; *Lehrbuch*, 1, 116—117), even when outwardly identical with Gerhardt's "chemical types," were in reality "mechanical types": that is, they were based solely on the valency of the constituent elements. Thus, whereas Gerhardt classed the hydrogen type, HH, and the hydrochloric acid type, HCl, as distinct *chemical* types, Kekulé, looking upon them as *mechanical* types, regarded the latter as merely a special case of the former. Applying this to the matter under consideration, it is evident, that, if Kekulé had employed Gerhardt's types, he could not have tabulated the foregoing compounds in the way he did, as they would not have belonged to the same type. Thus, if he had followed Gerhardt, marsh gas would have belonged to the hydrogen type, methylic chloride to the hydrochloric acid type, and so on; and the parallelism which Kekulé wished to indicate would have been completely hidden. It was, therefore, necessary for him not merely to tabulate the compounds on the marsh gas type, but, seeing that he had used the word "type," to obviate any possible misunderstanding by stating that he did not mean Gerhardt's types.*

* Kolbe also argues (*loc. cit.*) that, in the passage just quoted, Kekulé refers marsh gas to the chloroform type, not chloroform to the marsh gas type. To

The foregoing demonstration of the tetravalency of the double equivalent of carbon, C_2 (which, as we have seen, meant for Kekulé the atom C = 12), is obviously incomplete, as it holds good only for the limited class of compounds derivable from methane by the replacement of the hydrogen atoms by the same number of monad radicles. It contains no suggestion of the law of mutual linking of carbon atoms and can at most be regarded as the germ of Kekulé's later theory.

In the same year, Kekulé published an important theoretical paper: "On the So-called Conjugated Compounds and the Theory of Polyatomic Radicles" (*Annalen*, 1857, **104**, 129). As the question is entirely one of valency and there are no experimental results to state, he uses Gerhardt's atomic weights, although in three experimental papers published the following year he again reverts, for the last time, however, to the old equivalents. In the introduction to the paper he states that the views which he advocates have, in great part at least, no claim to originality: they are an extension of ideas incidentally put forward by Williamson and forming what might be termed his "theory of polyatomic radicles"; ideas which had already been extended by Odling in his paper "On the Constitution of Acids and Salts," and which had been adopted, although not in a strict form, by Gerhardt in the fourth volume of his *Traité*. Kekulé divides the elements into monobasic or monatomic, dibasic or diatomic, and tribasic or triatomic, and points out that the three principal types—hydrogen, water and ammonia—follow from this classification. In a footnote he adds (*loc. cit.*, p. 133): "Carbon is, as may easily be shown, and as I shall explain in detail on a later occasion, tetrabasic or tetratomic: that is, 1 atom of carbon C = 12 is equivalent to 4 atoms of H." He shows that, as regards the so-called conjugated compounds, there is no need to refer these to a separate class: their constitution may be expressed in terms of the valency of the radicles, simple and compound, which they contain. We have already seen, however, that this view of the nature of conjugated compounds had been clearly stated by

disprove this it is only necessary to point out that in the table of compounds which "may be referred to the same type," the formula of chloroform is given *under* that of marsh gas. Kolbe apparently understands the words "referred to the same type" to mean "referred to the same type as chloroform," whereas the sense is: "may all be referred to one and the same type," namely the type that heads the list. This is clearly shown both by the context and by the way in which the words "same type" are again used after the table of compounds.

Kolbe put himself completely out of court in any discussion involving a knowledge of Kekulé's writings, by the statement that he did not consider them worthy of serious attention. In his historical study: *Meine Betheiligung an der Entwickelung der theoretischen Chemie* (*J. pr. Chem.*, 1881, [ii], **23**, 377) he says: "In this connection I have had occasion for the first time to read attentively Kekulé's *Lehrbuch*, especially the historical and theoretical chapters. Until then, I had only glanced hastily through it, as I perceived that I could learn nothing useful from it."

Frankland in 1852. Kekulé, starting, as he premises, with the theory of multiple types and mixed types containing polyvalent radicles, as expounded by Williamson and Odling, develops it into a complete system, laying special stress on the fact that these classes of types are possible only when such polyvalent radicles are present. Thus, of compounds containing the divalent radicle SO_2, he gives:

	Type.		
I.	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$ $\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\SO_2''\\H\end{matrix}\right\}O$ Sulphuric acid.	$\left.\begin{matrix}C_2H_5\\SO_2''\\H\end{matrix}\right\}O$ Hydrogen ethylic sulphate.
II.	$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\SO_2''\\H\end{matrix}\right\}O$ Sulphurous acid.	$\left.\begin{matrix}C_6H_5\\SO_2''\\H\end{matrix}\right\}O$ Benzenesulphonic acid.
III.	$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right.$		$\begin{matrix}C_6H_5\\SO_2''\\C_6H_5\end{matrix}$ Diphenylsulphone.

"Compound radicle" is understood in Gerhardt's sense of "a residue left unattacked in any particular reaction," and the "basicity" (valency) of these radicles is deduced from the number of atoms, greatly differing from the radicles themselves in chemical character, with which they combine.

This introduction of the radicles into the types, which must at the time have appeared to place the type theory on a firm basis, was destined to render that theory unnecessary.

Another point worthy of note is the way in which Kekulé uses the action of the chlorides of phosphorus to distinguish between the water type and the hydrogen type. Developing an idea to be found in his memoir on thiacetic acid, he points out, that, in the case of the water type, two atoms of chlorine replace one atom of typical oxygen, causing the compound to break up into two atomic groups, whereas the hydrogen type is not acted upon and remains intact. Thus

$\left.\begin{matrix}C_2H_5\\SO_2'\\H\end{matrix}\right\}O$ yields $\dfrac{\begin{matrix}C_2H_5,Cl\\SO_2'',Cl_2\end{matrix}}{H,\ Cl}$

whereas

$$\left.\begin{matrix} C_6H_5 \\ SO_2'' \\ H \end{matrix}\right\} O \qquad \text{yields} \qquad \begin{matrix} C_6H_5 \\ SO_2'', Cl \\ H, Cl \end{matrix}$$

In the foregoing paper, Kekulé accepts the radicles (residues) in the form in which he received them from his predecessors and empirically deduces their valency from a study of their compounds. In his great theoretical paper, published the following year (*Annalen*, 1858, **106**, 129), "On the Constitution and Metamorphoses of Chemical Compounds, and on the Chemical Nature of Carbon"—a paper which is the foundation of our present theories of organic chemistry—he goes to the root of the matter. He says:—

"I regard it as necessary and, in the present state of chemical knowledge, as, in many cases, possible, to explain the properties of chemical compounds by going back to the elements themselves which compose these compounds. I no longer regard it as the chief problem of the time, to prove the presence of atomic groups which, on the strength of certain properties, may be regarded as radicles; and in this way to refer compounds to a few types, which can hardly have any significance beyond that of mere pattern formulæ. On the contrary I hold that we must extend our investigation to the constitution of the radicles themselves; that we must ascertain the relation of the radicles to one another and, from the nature of the elements, deduce both the nature of the radicles and that of their compounds.'

He then points out how the conception of the valency of the different elements may be utilised for this purpose. In this connection he further develops his ideas on the tetravalency of carbon, and gives the list of compounds: CH_4, CCl_4, CH_3Cl, $CHCl_3$, $COCl_2$, CO_2, CS_2, CNH, pointing out that "the sum of the chemical units combined with one atom of carbon is 4. This leads to the view that carbon is *tetratomic* (or tetrabasic)." At this point he introduces (*loc. cit.*, p. 153, footnote) a passing reference to the advantage of referring compounds to the marsh gas type: "If carbon is introduced as a *tetratomic radicle* among the types, several already known compounds may be formulated in a relatively simple manner."

He next proceeds to discuss the question of the linking of carbon atoms with one another:

"In the case of substances which contain several atoms of carbon, one must assume that some at least of the atoms are held in the compound in the same way [as in the cases already quoted] by the affinity of the carbon, and that the carbon atoms themselves are attached together, whereby a portion of the affinity of the one carbon atom is of course held in combination by an equal portion of the affinity of the other.

"The simplest and therefore most probable case of this union of two carbon atoms is that in which one unit of affinity of the one carbon atom is combined

with one unit of affinity of the other. Of the 2×4 units of affinity of the two carbon atoms, two are used up in holding the two atoms together; there therefore remain six which may be held in combination by atoms of other elements. In other words the group C_2 is hexatomic. . . . . .

"If more than two carbon atoms unite in the same way, the basicity of the carbon group will be increased by two units for each fresh carbon atom. Thus the number of hydrogen atoms (chemical units) which may be combined with n carbon atoms is expressed by

$$n(4-2)+2=2n+2.$$

". . . . Up to this point we have assumed that all the atoms attaching themselves to carbon are held by the affinity of the carbon. It is equally conceivable, however, that in the case of polyatomic elements (O, N &c.) only a part of the affinity of these—for example, only one of the two units of affinity of the oxygen, or only one of the three units of the nitrogen—is attached to carbon; so that one of the two units of affinity of the oxygen, and two of the three units of affinity of the nitrogen, remain over and may be united with other elements. These other elements are therefore only in indirect union with the carbon, a fact which is indicated by the typical mode of writing the formulæ:

$$\left.\begin{matrix} C_2H_5 \\ H \end{matrix}\right\} O \qquad \left.\begin{matrix} C_2H_5 \\ H \\ H \end{matrix}\right\} N \qquad \left.\begin{matrix} C_2H_3O \\ C_2H_5 \end{matrix}\right\} O \qquad \left.\begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix}\right\} N.$$

"In like manner the carbon groups are held together by the oxygen or the nitrogen."*

He points out that a great many organic compounds may be formulated on the basis of the "simplest" attachment of carbon to carbon, but that, in others which contain more carbon in proportion the "next simplest" attachment may be assumed, involving a closer union of the carbon atoms. He does not, however, go into details regarding the principles to be adopted in formulating such unsaturated compounds.

It is to be noted that at that time Kekulé still held Gerhardt's view that rational formulæ were merely an expression of chemical reactions. The idea that it was possible to express the relative positions of the atoms within the molecule was of later growth.

Kekulé had by his interpretation of the types in terms of the law of valency, and by his dissection of the compound radicles in accordance with the same law, superseded both the type theory and the radicle

* As a further example of how little Kolbe thought it necessary to master the details of theories he set himself to criticise, the following passage may be quoted, in which, after making merry over the expression "carbon skeleton," used by Kekulé in the foregoing paper, he says (*J. pr. Chem.*, 1881, [ii], **24**, 407): "If I am not mistaken, it is assumed that *all* organic compounds which contain more than one atom of carbon possess such carbon skeletons. Where, then are we to place the cacodyl compounds, trimethylamine, trimethylsulphine iodide and other organic substances?"

theory, except so far as they might be useful for purposes of exposition. Nevertheless, partly as a concession to the prevailing usage of his school, and partly, doubtless, from force of habit, he continued for a long time to write typical formulæ. This led to a somewhat mechanical mode of formulation, occasionally attended with misleading results. Thus, in the paper just quoted (pp. 145—146), we find benzene formulated on the hydrogen type and benzoic acid on the water type,

$$\left.\begin{matrix}C_6H_5\\H\end{matrix}\right\} \qquad \text{and} \qquad \left.\begin{matrix}C_7H_5O\\H\end{matrix}\right\} O,$$

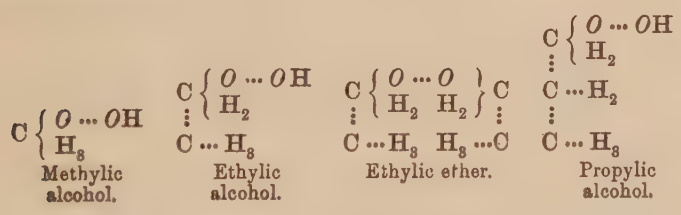
which leads him to state that, in the sulphonation of benzene, it is the typical hydrogen, but, in that of benzoic acid, hydrogen of the radicle, which is replaced, and to assign these reactions to two distinct categories. Again the hydroxy-acids are formulated on the double water type; thus lactic acid is $\left.\begin{matrix}C_3H_4O''\\H_2\end{matrix}\right\} O_2$; a mode of representing these substances which obliterates the distinction between the acidic and the alcoholic hydrogen atoms, and was responsible for the errors into which Wurtz fell in the earlier part of his well-known controversy with Kolbe. Kekulé himself is perfectly clear about the difference between these two typical hydrogen atoms and explains its cause with all possible precision (*Lehrbuch*, 1, 731); nevertheless he quotes the formula $\left.\begin{matrix}C_3H_4(HO)O\\H\end{matrix}\right\} O$ for lactic acid (first put forward in the old equivalents by Kolbe) only to reject it with the remark (*loc. cit.*, p. 736): "Such formulæ offer no advantages over the typical formulæ; on the contrary they conceal a great number of analogies and, in other cases, cause analogies to be suspected where none exist." I venture to think that I have just shown that the typical formulæ are not quite free from these defects. As regards the particular case of the formula of lactic acid, there is no doubt that the reluctance which Kekulé and his school at that time displayed to make use of the hydroxyl group in formulating compounds was an effect of Laurent's supposed burlesque proof of the existence of the radicle *eurhyzene*, that is, hydroxyl (see Laurent's *Chemical Method*, Odling's translation, p. 293). I say "supposed burlesque," because, at the present day, there is probably no chemist who has occasion to refer to "the hydroxyl-group"—which, in chemical compounds, is an abstraction and, in certain electrolytic dissociations, an entity—but would willingly subscribe, in all seriousness, the words which Laurent wrote in jest.*

* When, however, Kekulé (*Lehrbuch*, 1, 736, footnote) quotes Laurent's *eurhyzene* as a proof that Kolbe's view of the constitution of the acids of the lactic series as hydroxy-derivatives of the acids of the acetic series, is not original, one can only surmise that he was infected by Laurent's spirit of elaborate pleasantry.

This adherence to the outward form of the typical formulæ was, however, a minor defect, especially as Kekulé showed in his *Lehrbuch* how, by means of his graphic formulæ, the relations of the different atoms to one another within the molecule might be clearly exhibited. The graphic symbols were, however, as Kekulé himself pointed out, too cumbrous for ordinary use; they shared the fate of Dalton's atomic symbols and had to yield to the superior simplicity of those of Berzelius, which, with a few additions in the shape of bonds and valency marks, were found to satisfy all requirements. Even the circles with which Crum Brown, in his system of graphic formulæ, at first surrounded the symbols, were soon discarded.

Kekulé's models of atoms, on the other hand, to which reference will be made later, had a brilliant future before them.

It must be mentioned that, shortly after the publication of Kekulé's paper on the constitution of chemical compounds, analogous views were put forward independently by Couper (*Ann. Chim. Phys.*, 1858, [iii], **53**, 469; *Phil. Mag.*, 1858, [iv], **16**, 104). The two investigators followed different paths, and their results were in some respects different. Kekulé accepted the type theory and furnished it with a philosophical basis by explaining the existence of the pattern formulæ, or types—simple, multiple, and mixed—by means of the valency of the constituent elements; Couper, on the other hand, rejected the type theory altogether, and, starting with the idea of the valency of the elements, proceeded to construct constitutional formulæ for various compounds. Couper held peculiar views on the subject of the atomic weights: thus, whilst carbon was C = 12, oxygen was only *O* = 8. Carbon was tetradic; and the small oxygen atoms were dyadic, but were supposed always to occur linked together in pairs, so that the resulting group, *O* ··· *O*, as Couper wrote it, was also dyadic, and was therefore, to all intents and purposes, identical with the dyadic O = 16. The following formulæ will illustrate his system:



Couper's formulæ are thus, in spite of the peculiarity in the mode of writing oxygen, nearer to our present formulæ than those used by Kekulé at that period, and from the manner in which he discusses them it is evident that he intends them to be constitutional formulæ and not mere "formulæ of double decomposition" such as were employed by Gerhardt's school. The constitution assigned to the foregoing compounds is, however, identical with that previously proposed by Kolbe, with a difference, however, in the mode of writing the formulæ.

Kolbe (*J. pr. Chem.*, 1881, [ii], **23**, 366) and Frankland (*Proc. Roy. Soc.*, 1865, **14**, 198) claim to have anticipated Kekulé's enunciation of the tetravalency of carbon in a paper which they * published in 1857 (*Annalen*, 1857, **101**, 262 *seq.*). This claim, however, cannot be sustained, unless we ignore the list of compounds formulated on the marsh gas type, which Kekulé drew up in his paper on mercuric fulminate published a short time previously. Kolbe, indeed, gave what he considered to be reasons for ignoring this list; but I believe I have shown (p. 123) that these supposed reasons are based on a misunderstanding of Kekulé's meaning. Kolbe and Frankland's paper appeared so soon after Kekulé's that there can be no doubt of their having arrived at their conclusions quite independently of Kekulé, the more so as these conclusions are drawn entirely from their own work. Moreover, as the whole paper deals with the application of the law of valency, discovered by Frankland, to the interpretation of the constitution of organic compounds, it is clear that the authors had the tetravalency of carbon, or rather the tetravalency of the double equivalent, C_2, in their minds, although they did not mention it in so many words. Frankland had already shown (*v. supra*) how cacodylic acid might be derived from arsenic acid, or, strictly speaking, how the hypothetical cacodylic anhydride might be derived from arsenic anhydride, by replacing two equivalents of oxygen by two of methyl. Kolbe and Frankland now apply this view to the hydrated acids: thus from

$3HO,AsO_5$	$2HO,S_2O_6$	$2HO,C_2O_4$
Arsenic acid.	Sulphuric acid.	Carbonic acid.

they deduce

$HO,(C_2H_3)_2AsO_3$	$HO,(C_2H_3)S_2O_5$	$HO,(C_2H_3)C_2O_3$
Dimethylarsenic (cacodylic) acid.	Methylsulphuric (methylsulphonic) acid.	Methylcarbonic (acetic) acid.

* Through inadvertence this paper appeared under Kolbe's name only (compare Frankland's *Experimental Researches*, p. 148). Except in the opening sentences, in which Kolbe is referring to previous work of his own, the pronoun "we" is used throughout as denoting the joint authors.

They point out that, for each atom (equivalent) of oxygen which is replaced by methyl, one equivalent of water *HO* is simultaneously removed, so that for each introduction of a methyl group the basicity of the acid is reduced by 1. By replacing a further atom (equivalent) of oxygen in acetic acid by hydrogen or by methyl and again simultaneously removing *HO*, they obtain

$\left.\begin{matrix} C_2H_3 \\ H \end{matrix}\right\} C_2O_2$ and $\left.\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right\} C_2O_2$

Aldehyde Acetone

which are no longer acids at all. Further on, in the same paper, they point out that carbonic acid may be formulated $2HO,(C_2O_2)O_2$, and that it is the two "extra-radical" oxygen atoms which are replaced by methyl, each carrying with it an equivalent of water.

If we translate this into modern atomic weights, each "extra-radical" equivalent of oxygen, plus an equivalent of water, represents a hydroxyl group: $O + HO(O = 8) = OH(O = 16)$; so that the above formula for carbonic acid is identical with $CO(OH)_2$. It is thus hydroxyl of the hypothetical carbonic acid, and not, as the authors suppose, oxygen of carbonic anhydride, which is replaced by methyl or hydrogen in the foregoing mode of deducing acetic acid, aldehyde, and acetone from carbonic acid.

The tetravalency of the double equivalent of carbon, C_2, is certainly implied in Kolbe and Frankland's paper; but, as already mentioned, it is nowhere expressly stated, and one may be permitted to doubt whether many chemists could at that period have disentangled the doctrine from the very complicated hypothesis in which the use of the old equivalents had compelled the authors to involve it. Those who profited most by the work were those who could translate it into Gerhardt's atomic weights, and probably Kekulé and his school were more indebted to it than they were at that time conscious of. It is clear, however, that the paper contains no hint of the linking of carbon atoms, as this conception could not be developed in terms of Gmelin's equivalents. Indeed, so far as Kolbe was concerned, even after he had accepted the new atomic weights, he continued, to the end of his life, to cast ridicule on this conception (compare *J. pr. Chem.*, 1881, [ii], **24**, 414).

That Kolbe and Frankland's work on the tetravalency of carbon did not, therefore, exercise a direct and immediate influence in any degree comparable with that produced by Kekulé's great paper on the same subject, is to be ascribed to the fact that their conclusions were stated in terms of an inconsistent scheme of atomic weights. We must not forget, however, that the same principle, namely, that of the

derivation of organic acids, aldehydes and ketones from carbonic acid, led Kolbe, later on, to the prognosis of secondary and tertiary alcohols, of which triumph of theoretical foresight the germ is contained in the concluding paragraph of Kolbe and Frankland's paper (compare *Annalen*, 1857, 101, 265).

I have already referred to Kekulé's models of atoms. The conception which he introduced in these, as to the distribution of the four affinities of the carbon atom, has led to most important results. He begins by referring (*Zeitschr. f. Chem.*, 1867, *N.F.*, 3, 217) to the imperfections of his original system of graphic formulæ and of the models based upon them, and further points out that models constructed on the basis of Crum Brown's graphic formulæ and consisting of spheres with rods radiating from them in one plane, do not really express more than the graphic formulæ themselves, inasmuch as the representation which they afford of a space formula is only apparent, the atoms being all in the same plane; and that, unless the rods are bent or arbitrarily displaced, certain combinations, *e.g.* triple bonds between carbon atoms, cannot be represented by them at all. He then proceeds to describe a model of the carbon atom which he has devised and which avoids these difficulties: "The four units of affinity of the carbon atom, instead of being placed in one plane, radiate from the sphere representing the atom in the direction of hexahedral axes, so that they end in the faces of a tetrahedron. . . . A model of this description permits of the union of 1, 2 and 3 units of affinity, and, it seems to me, does all that a model can do."

Even while making this apparently sweeping statement, Kekulé can hardly have realised the part that this model was destined to play in the development of theoretical chemistry; how in van't Hoff's hands it was to be the means of tracing the subtle asymmetry which Pasteur had deduced from the optical behaviour and the crystalline form of certain organic compounds, back to the asymmetric structure of the molecule itself; of explaining the mysterious isomerism of fumaric and maleic acid, which had baffled Kekulé's own acumen; and of laying down the space conditions of existence or non-existence of the closed-chain compounds of which Kekulé himself had introduced the conception into chemistry in his benzene theory.

I have already referred to Kekulé's benzene theory as the crowning achievement of the doctrine of the linking of atoms. To give a complete account of this theory and of the criticisms to which it has been subjected, would far exceed the scope of the present lecture; whilst to treat it briefly may seem superfluous, as the theory, in its main outlines, is familiar to every one with even the most elementary knowledge of organic chemistry.

This theory was first published in 1865 in the *Bulletin de la Soc. Chimique* (1, 98). I quote, however, from the fuller account published a year later in Liebig's *Annalen* (1866, 137, 129).

In this paper, "On the Constitution of the Aromatic Compounds," Kekulé begins by stating that none of the chemists who have dealt with the subject of benzene and its derivatives, have attempted to deduce the constitution of these compounds from the tetravalency of carbon and that some have gone so far as to state that this cannot be done. He then enumerates various distinguishing characteristics of the benzene compounds: amongst others, that there is no benzene compound containing fewer than six carbon atoms. After pointing out that six carbon atoms might be linked together by alternate single and double bonds, he says:

"If one assumes that six carbon atoms are attached to one another according to this law of symmetry, one obtains a group which, regarded as an *open chain*, contains *eight* unsaturated units of affinity. By making the further assumption that the two carbon atoms at the ends of the chain are linked together by one unit of affinity each, a *closed chain* (a symmetrical ring) is obtained which still contains *six* unsaturated units of affinity.*

"From this *closed chain* all the substances usually designated as 'aromati compounds' are derived. . . .

"In all aromatic substances a common nucleus may be assumed: it is the closed chain C_6A_6 (in which A denotes an unsaturated affinity).

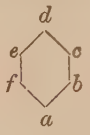
"The six affinities of this nucleus may be satisfied by six monatomic elements. They may also, wholly or at least in part, be satisfied by one affinity of polyatomic elements, the latter necessarily bringing with them other atoms into the compound, thus producing one or more *side chains*, which in their turn may be lengthened by the addition of other atoms.

"The satisfying of two affinities of the nucleus by one atom of a diatomic element, or of three affinities by one atom of a triatomic element, is, according to the theory, impossible. Compounds of the molecular formulæ, C_6H_4O C_6H_4S, C_6H_3N, are, therefore, unthinkable."

Here we meet for the first time (if we except Kekulé's preliminary note on the same subject) with the now familiar expressions "closed chain," "nucleus," and "side chain," without which it would, at the present day, be impossible to discuss the problem of the constitution of the benzene compounds. The last paragraph quoted is worthy of note: it contains a very positive statement on a point which does not appear to follow with absolute necessity from the formulæ which Kekulé uses. It involves conceptions regarding the actual distribution of the atoms in space; and the conclusion at which Kekulé arrives suggests that he was already using the space-models of atoms which he described two years later.

* In the original paper these atomic groups are represented by means of Kekulé's graphic formulæ.

He points out that the foregoing constitution of the benzene nucleus involves the equivalence of the six unsatisfied affinities and proceeds to deduce the number of possible substitution derivatives of benzene, containing 1, 2, 3, &c., identical substituents, the isomerism depending on the relative positions of the substituents towards one another. Amongst other things he points out that whereas there are only three substitution derivatives possible of the general formula $C_6H_3X_3$, there are six of the formula $C_6H_3X_2Y$. In stating this conclusion he makes use of a hexagon lettered as follows



and says: "For dibromnitrobenzene, for example, there would be the following forms:

"(1) For *a b c*: $C_6H_3BrBr(NO_2)$
$C_6H_3Br(NO_2)Br$
(2) For *a b d*: $C_6H_2(NO_2)HBr_2$
$C_6H_2BrH(NO_2)Br$
$C_6H_2BrHBr(NO_2)$
(3) For *a c e*: $C_6HBrHBr(NO_2)$."

It was this series of compounds that Körner used later (*Gazzetta*, 1874, **4**, 305) in his well-known method for the orientation of the bromine atoms in the dibromobenzenes.

The homologues of benzene are discussed. "The homology may depend either upon an increase in the number of the side chains, or on the lengthening of side chains the number of which remains the same." Thus there ought to be three dimethylbenzenes (only one was at that time known) and, isomeric with these, the synthetical ethylbenzene of Fittig and Tollens.

The law of oxidation of the homologues of benzene is laid down: namely, that each hydrocarbon side chain, no matter how many carbon atoms it may contain, is oxidised away, with the exception of the carbon atom attached to the nucleus, which remains in the shape of a carboxyl-group. The resulting acids thus contain as many carboxyl-groups as there were hydrocarbon side chains in the original compound. By more moderate oxidation intermediate products are obtained: thus, xylene and cymene both yield toluic acid. Moreover, the possibility is foreseen, in the case of side chains containing more than one carbon atom, of oxidising only a portion of the chain, and thus obtaining an acid in which the carboxyl is not directly attached to the nucleus.

The question of substitution in the nucleus and substitution in the

side chain is also gone into, and the difference in the character of the resulting derivatives is pointed out.

At the end of the theoretical portion of the memoir, Kekulé says, referring to different possible formulæ for benzene:

"A problem of this kind might at first sight appear quite insoluble; but I nevertheless believe that experiment will furnish a solution. It is only necessary to prepare, by methods as varied as can be devised, as great a number of substitution products of benzene as possible; to compare them very carefully with regard to isomerism; to count the observed modifications; and especially, to endeavour to trace the cause of their difference to their mode of formation. When all this is done we shall be in a position to solve the problem."

Could the course of subsequent investigation in this field have been more accurately laid down in advance?

Kekulé's memoir on the benzene theory is the most brilliant piece of scientific prediction to be found in the whole range of organic chemistry. What Kekulé wrote in 1865 has since been verified in every essential particular. Not only have the various substitution derivatives been discovered, in the number and with the properties required by the theory, but various observations which appeared to contradict this theory have been proved erroneous. Moreover, the theory has shown itself capable of boundless development. There seems to be no limit to the fruitfulness of Kekulé's conception of closed chains or cycloids. The extensions of the idea, of which extensions Erlenmeyer's naphthalene formula and Dewar's formulæ for pyridine and quinoline were amongst the earliest instances, have gone on increasing in a rapid geometrical ratio, until, at the present day, the literature dealing with cycloids, although of so recent growth, is more than twice as voluminous as that of the paraffinoids. To quote the words of the address which our Society presented to Kekulé on the occasion of the *Benzolfeier*: "This theory found the chemistry of even the immediate derivatives of benzene an almost untilled field; it has transformed it into a fertile province, to which have been annexed regions the very existence of which was unknown."

But even in the undeveloped state of the subject prior to Kekulé's theory, the facts were apparently so intricate and so unconnected that few chemists could claim to have mastered them. The theory appeared; the previously unmarshalled facts fell into their proper places; and not only this, but it was possible to say whether, in any given section of the subject, the facts were complete or only fragmentary. The increased ease in dealing with this branch of chemistry, the fascination of the numerous scientific problems which Kekulé's theory suggested, and lastly the economic importance of many of the benzene compounds and of other allied cycloids, attracted to this field

a crowd of workers, whose numbers, if they have not of late years actually increased, at least show no signs of diminishing. The debt which both chemical science and chemical industry owe to Kekulé's benzene theory is incalculable. As regards the former, three-fourths of modern organic chemistry is, directly or indirectly, the product of this theory; and as to the latter, the industries of the coal-tar colours and the artificial therapeutic agents, in their present form and extension, would be inconceivable without the inspiration and guidance which they have received and still receive from Kekulé's fertile idea.

Various points in Kekulé's theory which were at first either fundamental assumptions, or deductions from these fundamental assumptions, have since been experimentally proved: thus the equivalence of the six hydrogen atoms in benzene by Ladenburg, and the fact that there is, relatively to every hydrogen atom, a symmetrically situated ortho-pair and a symmetrically situated meta-pair, by Hübner and Petermann, Wroblewsky, and others.

The orientation of the substituents in the derivatives of benzene, merely indicated by Kekulé, has been successfully carried out by von Baeyer, Graebe, Ladenburg, Griess, and, above all, Körner. The concordant results obtained by the most diverse methods have placed this part of the subject on a sure foundation.

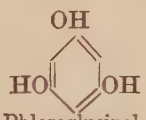
The non-identity of the two ortho-positions 1 : 2 and 1 : 6 in Kekulé's formula containing alternate double and single bonds, which is in contradiction to the proved identity of the two ortho-products and which would necessitate the existence of four isomeric disubstitution derivatives instead of three, has called forth much criticism. Kekulé sought to meet the difficulty by means of his well-known oscillation formula, in which the double and single bonds continually exchange places. This is virtually a return to the simple hexagon, given as an alternative formula by Kekulé in his original paper: the distribution of the unsaturated affinities is ignored.

Of the various formulæ which have been proposed in place of Kekulé's, I will mention Ladenburg's prism formula, Claus's diagonal formula, and Armstrong and von Baeyer's centrical formula. All of these agree with Kekulé's formula in connecting together six CH-groups by single bonds so as to form a closed chain; the disposal of the remaining six affinities is the point wherein they differ. Ladenburg's formula is seldom discussed at the present day. It represents the ortho-carbon atoms as not directly connected, thus ignoring the analogy between the ortho-position in benzene compounds and the α-position in paraffinoid compounds, and rendering the formulation of compounds like naphthalene and phenanthrene impossible, at least in accordance with the prevailing views. Moreover, the substitution of any two dissimilar groups for hydrogen would render carbon atoms of

the nucleus asymmetric, so that every compound of the general formula C_6H_4XY ought to exist in two enantiomorphous forms, whereas all efforts to isolate such forms have hitherto proved fruitless, benzene derivatives being optically inactive unless there is an asymmetric carbon atom in a side chain. Claus's diagonal formula was formerly objected to on the ground that the ortho- and para-positions were identical and that it therefore required the existence of only two di-substitution products. This difficulty has been got over by introducing spatial considerations and assuming that the greater distance between the para-carbon atoms, as compared with the ortho-, constitutes a difference. It is necessary, however, further to assume that the carbon and hydrogen atoms lie in one plane, otherwise asymmetric substitution derivatives would exist; and this assumption, taken in conjunction with that of para-bonds, would appear to demand the placing of the four affinities of carbon in one plane; in other words, it would involve the abandonment of van't Hoff's tetrahedron. The centrical formula is difficult to criticise; the mode of disposing of the central bonds is entirely without analogy and does not appear to be accessible to the test of experiment. In its application and predictions, the centrical formula is identical with Kekulé's simple hexagon.

The question of the disposal of these unsaturated affinities is, indeed, a very difficult one. Thus von Baeyer, who formerly opposed Claus's formula, has now, with certain limitations, adopted it (*Annalen*, 1892, 269, 177). According to him, it is impossible to devise a benzene formula which shall be applicable to all derivatives of benzene. He regards (*loc. cit.* p. 188) phthalic acid as derived from a benzene of Claus's formula and phloroglucinol from one of Kekulé's formula with alternate double and single bonds:

Phthalic acid.



Phloroglucinol.

Possibly the solution of this difficulty will be found when we possess a space formula capable of representing these various modes of distributing the unsaturated affinities as different desmotropic oscillation-phases of a ring of 6 CH-groups (compare Collie, Trans., 1897, 71, 1013). Of such a formula Kekulé's oscillation formula is a partial anticipation. Meanwhile chemists will doubtless continue to employ Kekulé's simple hexagon, without alternate double and single bonds, as a statical representation of the symmetry of the benzene molecule.

Various other important theoretical questions discussed by Kekulé might be mentioned here; but time does not permit.

If, in conclusion, we ask ourselves what is the characteristic note of Kekulé's theoretical creation, the chemistry of structure, I think we may reply that it is the treatment of the problem of isomerism—the problem which first necessitated the use of constitutional formulæ—as one of geometrical symmetry. Kekulé's formulæ, stripped of the fetters of the type theory with which he at first encumbered them, were, from one point of view, merely more or less symmetrical geometrical figures. In order to predict the number of substitution compounds, it was only necessary to consider the degree of dissymmetry of the parent compound: the less the symmetry, the greater the number of isomeric substitution compounds. The extraordinary fertility of this conception is shown by the development which it has undergone at the hands of van't Hoff, J. Wislicenus, von Baeyer, and others.

Kekulé's structural formulæ cleared away at one stroke the entire brood of pseudo-constitutional formulæ. If organic chemists no longer waste their time in wrangling over the question whether, for example, methylamine is methane in which one atom of hydrogen is replaced by the amido-group, or ammonia in which one atom of hydrogen is replaced by methyl, the merit is Kekulé's.

The accuracy of Kekulé's predictions has done more to inspire a belief in the utility of legitimate hypotheses in chemistry, and has therefore done more for the deductive side of the science, than that of almost any other investigator. His work stands pre-eminent as an example of the power of ideas. A formula, consisting of a few chemical symbols jotted down on paper and joined together by lines, has, as we have just seen, supplied work and inspiration for scientific organic chemists during an entire generation, and affords guidance to the most complex industry the world has yet seen.

Although much research remains to be done on the lines laid down by Kekulé, yet other problems are clamouring for solution, and other methods of investigation have been called into existence to solve them. The younger generation of chemists are, fortunately, labouring diligently in the field of physico-chemical research, which the organic chemists, occupied with questions of chemical structure, had perhaps unduly neglected. One problem, however, which, in many points at least, still awaits the physical chemist, is the correlation of his results with those of the structural chemist. When this is fully accomplished, there will be a debt of gratitude on both sides; but no one will be entitled to more gratitude than August Kekulé.

Seinem lieben Prof. Thorpe
mit herzlichsten Grüssen von
Haus zu Haus
Victor Meyer

VICTOR MEYER MEMORIAL LECTURE.

(Delivered on February 8th, 1900).

By T. E. Thorpe, Ph.D., D.Sc., LL.D., F.R.S., President of the Chemical Society.

By the untimely death of Victor Meyer, on August 8th, 1897, under circumstances of peculiar sadness, and at the comparatively early age of forty-nine, our sister Society in Berlin lost her President of the year, and, at the same moment, we were deprived of one of the most brilliant of that band of eminent men whom we distinguish as our Honorary Foreign Members. The Council have deemed it fitting that the attempt should be made to put on record our appreciation of the remarkable services Victor Meyer rendered to the science which he cultivated, during the all too short period of his activity, with such striking assiduity and success. As a friend of nearly thirty years' standing, and as one who worked, literally, side by side with him in the famous laboratory which he lived to direct, and died whilst directing, I have charged myself with the execution of this duty.

Of Meyer's early life—that is, of the period before I first knew him at Heidelberg as a girlish-looking, bright-eyed youth, quick of movement and active in thought, ready and fluent of speech, full of zeal, and intensely interested in the higher work of the place—I know little, beyond that he was born in Berlin and was the son of a calico manufacturer.* Once, in the course of some discussion on the characteristic differences in the school training of English and German lads, he made reference to his own experiences in the gymnasium, from which I gathered that his inclination towards science was in nowise shaped by what he saw or heard in early youth. Nor, so far as can be determined, was there anything in his home life which inclined him to take to chemistry. In the case of many who have become eminent in physical science—and doubtless also in the case of more who have not—their first love has sprung from the passion of experimenting. But at this time Meyer, apparently, had neither the opportunity nor the desire to make experiments. Indeed, the home atmosphere tended to make him literary or artistic. There can be no doubt that he owed to this environment, and more especially to the example and precept of his mother, herself a woman of considerable intellectual power, certain strongly marked features of character which

* The date of his birth was September 8th, 1848,

are not usually associated with men of science. According to his friends Liebermann and Jacobson, his own wish was to become an actor, and that he would have succeeded in such a profession is highly probable. He had, indeed, all the natural gifts of the born actor—dramatic sense, emotional power, a fine voice, an impressive manner, and a handsome presence. When he became a teacher of chemistry, these attributes were turned to good account. His early love of declamation, combined with his elocutionary ability, eventually made him one of the most striking and effective lecturers in Germany. The traditions of the University lecture-theatre no doubt exercised their restraining influence, but Meyer was too much under the sway of his artistic temperament and too impatient of conventionality to repress altogether his natural bent. Moreover, he was not insensible to the effect he created, or unmindful of the influence he gained, when, to use the common phrase, he "let himself go," and by his trenchant, impressive language, and the brilliancy of his illustration, communicated something of his own enthusiasm to even the most listless of back-bench men. This power of exposition was quickly perceived, and no doubt its early recognition served to bring him the more speedily to the front.

At Heidelberg, as in many other centres of chemical instruction, there was a small Chemical Society, composed of the Extraordinary Professors, the Privat-docenten, and assistants, together with the senior or more active students in the various laboratories who were elected into it by favour of the teachers. In my time it numbered amongst its members Erlenmeyer, Ladenburg, Horstmann, Ludwig, Cohen (the mineralogist), Rose, and Emmerling. Its president was Bunsen, and the occasions on which he took the chair were the red-letter days of the session. We invariably sent him home happy, his pockets filled with all the good champagne corks we could collect. The formal business of the Society—if formal it can be called—was preceded by an *Abendessen*, and if not accompanied, at least succeeded, by a considerable manifestation of "das gemüthliche Element." No man was more popular at these gatherings than Meyer. His nimble mind and retentive memory, his gift of ready speech, his sense of humour and genial manner combined to make it pleasant to listen to him no matter whether he was, in accordance with the rules of the Society, called upon to give an account of some work which had just been published, or whether he was discussing and criticising a communication from a fellow member. From time to time we had reports of the condition of such investigations as were in progress in the Heidelberg laboratories, or of which the results were to appear in the forthcoming issue of the *Annalen*, for, at the period of which I write, the *Berichte* was a thin and puny publication, hardly out of its swaddling clothes, and with little sign of the

vitality which has since enabled it to assimilate practically the whole outcome of German chemical activity.

Of his own laboratory work, we had nothing from Meyer, for there was little or nothing at the time to be told. He had entered the University in the autumn of 1865, when barely seventeen years of age, and apparently with no very definite conception of a career. Suddenly he elected to study chemistry, and attached himself to Bunsen with the idea of ultimately becoming a teacher. It is not improbable that his choice was in a measure determined by the circumstance that he had attended some of Hofmann's lectures in Berlin in the preceding summer, and had thus been influenced by that great teacher, then in the fulness of his intellectual vigour. Those were the palmy days of Heidelberg—the days of Bunsen, Kopp, Kirchhoff, Helmholtz—and Meyer came under the spell of them all. His progress as a student was exceptionally rapid, and the brilliant manner in which he gained his doctorate—without the adventitious aid of a thesis—strongly impressed the whole philosophical faculty. Bunsen, especially, was greatly struck with the power and promise of the young Jew, then one of the youngest students in the University, and soon selected him as one of his assistants. It was in this capacity that I first made the acquaintance of Meyer. Bunsen for some years previously had been engaged in the examination of the mineral waters of South Germany, and Meyer at the time I entered the Heidelberg laboratory was acting as water analyst. However great the disciplinary value of such work might be (and no one who has practised Bunsen's method of water analysis, with its system of check and control, can doubt that it is one of the most rigorous quantitative exercises possible), I fear it was not altogether congenial to the active mind of the young assistant, who was yearning to try his 'prentice hand at original research. Accordingly, towards the end of 1868 he threw up the position, and entered Baeyer's little laboratory at the Gewerbeakademie in Berlin. Although in a sense overshadowed by the more magnificently appointed University laboratories of Hofmann in the Georgenstrasse, and of Kekulé in Bonn, both at that time comparatively new, the modest laboratory of the Gewerbeakademie, with its twenty workers, was already one of the most famous schools of organic chemistry in Europe. Baeyer himself had recently published his brilliant investigation of mellitic acid; and Graebe, at first alone, and subsequently in conjunction with Liebermann and with Caro, was at work on those remarkable series of inquiries which served to establish the true chemical nature and relationships of alizarin, and led eventually, with the independent collaboration of Perkin, to its artificial production on a commercial

scale. I well remember the interest and excitement which these discoveries created in Germany: they unquestionably gave an enormous impetus to the study of organic chemistry and attracted eager aspirants for chemical fame from all parts of the world, quickened, no doubt, by the perception of the rich promise of material benefit thus suddenly opened up. Heidelberg at that period was pre-eminently a school of inorganic chemistry: organic chemistry was represented by Delffs and was mainly studied by prospective apothecaries. Erlenmeyer had been called to the Polytechnic at Munich, and the influence of Kekulé's teaching was as yet hardly felt by any of the Privat-docenten.

Baeyer quickly recognised the power and ability of his pupil, and to Baeyer was undoubtedly due the impulse which started him on his career. As a "Vorgerückter" he attended no more lectures, and thus it happened that he who became one of the greatest organic chemists of his time never followed a course on organic chemistry. Shortly after his entrance into the laboratory, he began the series of half-dozen investigations which characterised his activity during his three years' stay in Berlin. His first paper, published in the *Berichte*, was a note on the action of trimethylamine upon monochlorhydrin, which substances form a basic condensation product, the chloride and the gold salt of which he described (*Ber.*, 1869, 2, 186). This was quickly followed by a short paper on diethyl thiodicarbonate, $S(CO_2Et)_2$, which he obtained by the action of ethyl chloroformate upon sodium sulphide (*Ber.*, 1869, 2, 297).

A far more ambitious production appeared in the following year, dealing with the constitution of the disubstituted benzenes (*Annalen*, 1870, 156, 265). In this memoir, Meyer described a new method of introducing a carboxyl group into the molecule of aromatic compounds, no matter whether the substance already contained a carboxyl group or not. This was effected by the action of sodium formate upon the potassium salt of the aromatic sulpho-acid.

Of the acids prepared synthetically by this method, isophthalic acid was the most important on theoretical grounds, as its production under these conditions led to a revision of the views then held with respect to the orientation of the radicles in the "ortho" and "meta" (salicylic) series. Isophthalic acid had been shown by Baeyer to be a 1 : 3-derivative. "Ortho"-sulphobenzoic acid, obtained from benzoic acid, was thought to have its radicles in contiguous positions. Meyer's experiments showed that isophthalic acid was the only dicarboxylic acid formed from the sulpho-acid by interaction with a formate, whence he argued that "ortho"-sulphobenzoic acid, and the chloro-, bromo-, nitro-, amido-, and hydroxy-benzoic acids corre-

sponding with it in constitution, must, like the isophthalic acid, be 1 : 3-derivatives. It followed that the "meta" (salicylic) series of compounds are the 1 : 2-compounds.

The main facts of this paper have long since taken their place in the history of our knowledge of aromatic compounds, but the memoir has an especial interest as being Meyer's first excursus into the realm of chemical theory. In a subsequent extension of the work, in conjunction with Ador (*Annalen*, 1871, 159, 1), he showed that in sulphanilic acid the substituent groups SO_3H and NH_2 were in the 1 : 4 positions. The phenolsulphonic acid from sulphanilic acid he proved to be identical with Kekulé's paraphenolsulphonic acid, and hence to have the position 1 : 4. Potassium monobromobenzoate fused with sodium formate yields isophthalic acid ; hence this bromobenzoic acid belongs to the 1 : 3 series. At the conclusion of their memoir, the authors gave a list of the disubstituted derivatives of benzene then known, arranged in columns according to whether the second substituent element or radicle is attached to the second, third, or fourth carbon atom, as deduced from the experimental evidence put forward. Their views as to the orientation of the substances there named, except in the case of the dihydroxybenzenes, have not been materially modified by subsequent inquiry.

Pending the publication of this work, Meyer essayed to solve that *arcanum* of aromatic chemistry, the constitution of camphor (*Ber.*, 1870, 3, 116). He sought to show in the first place that camphoric acid is a dicarboxylic acid, $C_8H_{14}(CO_2H)_2$. Since camphor yields, by the action of dehydrants, an homologue of benzene, namely, cymene, he reasoned that it must contain the benzene nucleus, and hence the remaining four carbon atoms must exist in the side-chains. But by the oxidation of camphor to camphoric acid, the side-chains apparently are not attacked ; the action would seem to be on two of the carbon atoms in the benzene ring. The carboxyl groups cannot be attached to one and the same carbon atom, otherwise camphor would not yield an homologue of benzene by abstraction of water. It would follow therefore that, in all probability, camphor ought to have the constitution expressed by one or other of the following formulæ :

(1) $COH \cdot C_8H_{14} \cdot CH.$

(2) $\underset{|}{C}(OH) \cdot C_8H_{14} \cdot \underset{|}{C}H.$

(3) $\underset{|}{C}H \cdot C_8H_{14} \cdot \underset{|}{C}H.$ (O bridge)

The first, or aldehydic, formula, suggested by Berthelot, was practically disproved by the work of Fittig and Tollens. The second formula, which contains the hydroxyl group, was rendered improbable by

Berthelot, and the improbability was further strengthened by Meyer, who found that acetic chloride was without action on camphor. The third formula then would seem of the three to be the most probable. The constitution of the group C_8H_{14} can only be inferred from that of the camphor cymene. This, as shown by Fittig and his pupils, is probably for the most part methylpropylbenzene.* Hence camphor would appear to have the constitution

$$\underset{\text{O}}{\overset{\text{CH}:\text{C}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{C}_3\text{H}_7):\text{CH}}{\overbrace{\qquad\qquad\qquad\qquad\qquad\qquad}}},$$

and camphoric acid

$$\text{CO}_2\text{H}\cdot\underset{\text{CO}_2\text{H}}{\underbrace{\text{C}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{C}_3\text{H}_7)\cdot\text{CO}_2\text{H}}}.$$

Borneol would be $CH(OH):C_8H_{14}:CH_2$. These views have now only an historical interest. All that is certain in them is that Meyer's conception of camphoric acid as a dicarboxylic acid is correct. The work of Claisen and Manasse has rendered it practically certain, as long surmised, that camphor has the grouping $C_8H_{14}<\begin{matrix}\text{CH}_2\\ \text{CO}\end{matrix}$. It has, however, required the labour of a generation of workers, and the accumulation of a literature which, as regards its bulk, is without a parallel in any other department of chemistry, to unravel the true relations of camphoric acid to camphor, and hence to get an insight into the constitution of a substance which has been known in Europe and prized as a medicine since the twelfth century.

Meyer acquired some experience in tuition, even in the early Heidelberg days, as a "coach," and in Berlin he added to his means, which were slender enough, by similar work. His success as a teacher induced Baeyer to recommend him to Fehling, who sought assistance, especially in modern organic chemistry and in laboratory teaching, in connection with his duties at the Stuttgart Polytechnic. His departure from Berlin was a great loss to the little circle in the Gewerbeakademie, where his high spirits and geniality made him universally popular. He was an omnivorous reader and the power of his memory was astonishing, so much so that on his leaving, Baeyer exclaimed "Jetzt werden wir ja wieder die Literatur nachschlagen müssen."

He remained in the Würtemberg capital barely a year. How he came to leave it has already been told by Professor Liebermann. Johannes Wislicenus had just been called from the Zürich Polytechnic to Würzburg, and the President of the school, Kappeler, was engaged in searching for a successor. He came to Stuttgart and, unknown to

* Widman (*Ber.*, 1891, **24**, 450) subsequently proved that cymene is methylisopropylbenzene, but this does not affect Victor Meyer's argument.

Meyer, attended one of his lectures. Although Kappeler, as he himself relates, knew little of chemistry, he was so struck with Meyer's power of lucid and stimulating exposition that the decision to invite him to Zürich was immediately made. At the close of the lecture, he communicated to the unsuspecting young teacher his idea, expressing, however, his fear that in comparison with his future students he might prove to be still too young. As Meyer laughingly promised to do his best, day by day, to repair this fault, the invitation was given, and thus, when barely 24 years of age, he found himself Ordinarius and Director of the chemical laboratory of the Zürich Polytechnic.

The Zürich Polytechnic has enjoyed a succession of distinguished teachers, and Meyer worthily sustained and, indeed, greatly extended the fame of its chemical chair. He was now in possession of a well equipped laboratory and surrounded by eager, active students, stimulated and encouraged by the enthusiasm of a teacher as active and eager, and, it may be added, as high-spirited as themselves. The thirteen years of Meyer's stay at Zürich constitute the most fruitful and the most brilliant period of his career: before its close, he had brought himself within the foremost rank of contemporary investigators. Some idea of his wonderful power of work, and of the stimulus he gave to others, may be gleaned from the fact that during that period the Zürich laboratory, under Meyer's direction, gave close upon 130 papers and memoirs to chemical literature. It is, of course, impossible here to do more than indicate, in the briefest possible outline, the outcome and significance of the more important of them.

During his short stay at Stuttgart he sent some half dozen papers to the *Berichte*, some of them in continuation of work which had occupied him in Berlin. The chief of these were put together in a memoir, in conjunction with Stüber, on the aromatic amines, which appeared in 1873 (*Annalen*, 1873, 165, 161). The main object of the work was to gain further evidence in favour of Meyer's view, that in the case of the chloro-, bromo-, iodo-, and nitro-derivatives of aromatic amines, obtained by direct substitution, it is always the hydrogen immediately contiguous to the amido-group which is replaced, or, in other words, that the NH_2 group exercises an attractive influence on the substituent. It was assumed by Kekulé that Riche and Bérard's dibromaniline, obtained by the reduction of dibromonitrobenzene, was identical with the dibromaniline from acetanilide. Meyer and Stüber proved that such was not the case. It was found that Riche and Bérard's dibromaniline yields, or is derived from, a *liquid* dibromobenzene, which boils at 219·4°, and remains liquid at −28°. Riese had previously obtained a liquid dibromobenzene boiling at 224° and crystallising below − 1°. All the three possible dibromobenzenes were thus made known. Meyer's

surmise that the new dibromobenzene was the 1 : 3 variety has since been established. The authors also made known the existence of a new tribromobenzene melting at 119°, the symmetric or 1 : 3 : 5-derivative. The isomerism of the liquid dibromobenzenes was subsequently conclusively demonstrated (*Ber.*, 1874, 7, 1560) by the crystallographic examination of their mononitro-derivatives by Groth and Bodewig.

In this connection may be mentioned a short paper, in conjunction with Wurster, "On some derivatives of solid Dibromobenzene" (*Annalen*, 1874, 172, 57). In the attempt to prepare a nitrated phenylenediamine by acting upon dibromonitrobenzene with alcoholic ammonia, in the same manner that Walker and Zincke obtained nitraniline from monobromonitrobenzene, they found that only a moiety of the bromine could be displaced, the resultant product being a new substance, bromonitraniline, in which the NO_2 group is next to the NH_2 group. By converting this substance into bromophenylenediamine, the two NH_2 groups would be in close proximity; on debrominating this compound, the resulting phenylenediamine was found to be identical with that discovered by Griess (m. p. 99°), whose surmise that the NH_2 groups were united to contiguous carbon atoms was confirmed.

Meyer began also an inquiry on the chemical nature of chloral hydrate, a substance which, in consequence of Liebreich's discovery of its anæsthetic action, had by that time become of considerable industrial importance, and was readily procurable. By the action of acetic chloride upon chloral hydrate, tetrachlorethyl acetate, $CCl_3{\cdot}CHCl{\cdot}O{\cdot}CO{\cdot}CH_3$, is obtained, identical with the product formed by the condensation of chloral and acetic chloride, or by the action of acetic chloride on acetaldehyde. Chloral alcoholate with acetic chloride yields $CCl_3{\cdot}CH{<}^{OC_2H_5}_{O{\cdot}CO{\cdot}CH_3}$, indicating that the alcoholate, as already shown by Henry on other chemical grounds, is the ethyl ether of trichlorethylidene glycol. By dissolving chloral hydrate in glacial acetic acid, Meyer obtained a white, crystalline substance, melting at 80°, which he regarded as isomeric with ordinary chloral hydrate (m. p. 55°).

The chloral hydrates may have respectively the constitution

(1) $CCl_3{\cdot}COH + H_2O$.
(2) $CCl_3{\cdot}CH(OH)_2$.

It is not proved, however, that they are not polymeric (*Annalen*, 1874, 171, 65). It is possible that the substance thus obtained is identical with the uniaxial form observed by Pope which slowly changes into the biaxial modification stable at ordinary temperatures (Trans., 1899, 75, 458). Meyer does not definitely

decide which of the two formulæ represents the constitution of ordinary chloral hydrate, but he inclines to regard it as trichlorethylidene glycol, which Perkin's observations on its magnetic rotation definitely indicate that it is.

Wallach's observation of the conversion of chloral into dichloracetic acid was shown by Meyer to be in accordance with a general property of aldehydes in alkaline solutions to take up the elements of water, one molecule of aldehyde being thereby reduced, whilst another is oxidised.

Meyer, in conjunction with his pupil Haffter, devised a very simple and rapid method of estimating the actual quantity of pure chloral in the commercial product, founded on the fact that chloral hydrate is rapidly decomposed by an aqueous solution of an alkali into chloroform and an alkaline formate (*Ber.*, 1873, 6, 600).

Although Meyer's papers up to this time had amply demonstrated his power of investigation, and afforded to critics like Kekulé and Baeyer abundant proof of the clearness and keenness of his vision, he had hitherto worked upon somewhat conventional lines. His memoir "On the Nitro-compounds of the Fatty Series" (*Annalen*, 1874, 171, 1), which appeared shortly after his removal from Stuttgart to Zürich, at once stamped him as an original investigator of a very high order. In anticipation that two series of alkyl nitrites would be found to exist, denoted in the methyl series by $CH_3 \cdot NO_2$ and $CH_3 \cdot O \cdot NO$, Meyer, whilst still at Stuttgart, had studied the action of amyl iodide upon silver nitrite and had obtained a colourless liquid, having the ordinary smell of amyl compounds, boiling between 150° and 160°, which on analysis was found to have the composition $C_5H_{11}NO_2$. Hence it was isomeric with amyl nitrite, a yellow liquid of a peculiar, disagreeable smell, which boils at 99°. To the new compound Meyer gave the name of nitropentane. The reaction was found to be general. He now entered upon an elaborate investigation of the nitro-compounds of the alkyl series and their derivatives, and of questions incidental to the main subject, which, in conjunction with his pupils, among whom may be mentioned Stüber, Rilliet, Chojnacki, Wurster, Constam, Janny, Lecco, Locher, Tcherniac, Ceresole, Müller, Demuth, Keppler, and Züblin, continued to occupy him at intervals for upwards of twenty years.

One peculiarity which distinguishes aromatic from aliphatic compounds consists in the ease with which 'nitration,'—that is, the replacement of hydrogen by the group NO_2 with the elimination of water—may be effected in the first-named substances. A reaction analogous to that by which nitrobenzene is formed from benzene was scarcely known among fatty compounds, the most familiar instance being the production of chloropicrin by the action of strong nitric

acid upon chloroform. The constitutional difference between the nitroparaffins, as the new group came to be called, and the alkyl nitrites consisted in the fact that, in the first-named substances, the NO_2 group is directly connected with a carbon atom, as in nitrobenzene, whereas in the alkyl nitrites the NO group is intermediately linked with the hydrocarbon radicle by means of oxygen. The alkyl nitrites are true esters capable of being resolved into alcohols and nitrous acid by the hydrolytic action of alkalis or acids. The nitroparaffins, on the other hand, are incapable of hydrolysis. By reduction, they yield alkyl hydroxylamines and then the corresponding amine. By reduction, however, the alkyl nitrites lose their nitrogen and form the corresponding alcohol.

Meyer's view that the nitroparaffins were veritable nitro-compounds was not at once accepted. Geuther, and subsequently Götting, assumed that nitroethane was acetamidoxide, $CH_3{\cdot}CO{\cdot}NH_2O$, whilst Kissel regarded it as acethydroxylamine, $CH_3{\cdot}CO{\cdot}NH(OH)$. It is true, as found by Meyer, that nitroethane, under the hydrolytic influence of strong acids, splits up into hydroxylamine and acetic acid, but since phosphoric chloride is without action upon nitroethane, an hydroxyl group must be assumed to be absent. As for Geuther's view of the constitution of these substances, Meyer had little difficulty in showing that it wholly failed to explain all their known reactions.

The general characteristics of the nitroparaffins, namely, the power of forming salts possessed by the primary and secondary compounds, the absence of this power in the tertiary series, together with the remarkable differences in the behaviour of bromine, and of the action of acids upon the primary and secondary nitroparaffins, were carefully studied by Meyer and his pupils. He found that when a solution of a primary nitroparaffin in potash is mixed with an alkaline nitrite and treated with sulphuric acid, the liquid acquires a blood-red colour which disappears on the further addition of acid. On shaking the whole with ether, there is obtained a solution of a new acid, known as a nitrolic acid, of the general formula $C_nH_{2n+1}{\cdot}C{<}^{N{\cdot}OH}_{NO_2}$. In the case of nitroethane, the formation of the ethylnitrolic acid may be represented as follows:

$$CH_3{\cdot}C{<}^{H_2}_{NO_2} + ON{\cdot}OH = H_2O + CH_3{\cdot}C{<}^{N{\cdot}OH}_{NO_2}.$$

That such is the constitution of ethylnitrolic acid is indicated by its formation by the action of hydroxylamine on dibromonitroethane,

$$CH_3{\cdot}C{<}^{Br_2}_{NO_2} + H_2N{\cdot}OH = 2HBr + CH_3{\cdot}C{<}^{N{\cdot}OH}_{NO_2}.$$

The nitrolic acids are colourless, sweet-tasting substances of a strong

acid reaction, readily soluble in water, and for the most part easily crystallisable. In alkaline solution, they give an intense blood-red coloration and form characteristic precipitates with salts of the heavy metals. They slowly decompose on standing, and on heating are quickly resolved into the corresponding fatty acid, nitrogen, and nitrogen dioxide. On treating the nitrolic acids with sodium amalgam, substances known as azaurolic acids are formed. They are strongly coloured, sparingly soluble substances, and differ from the corresponding nitrolic acid by containing two atoms of oxygen less. The best known member of the series is ethylazaurolic acid, $C_2H_4N_2O$, or more probably $C_4H_8N_4O_2$. On heating, it yields, together with formation of nitrous oxide and water, ethylleucazone, $C_4H_7N_3O$, a substance possessing both acid and basic properties, and in its general characteristics resembling an amido-acid.

The secondary nitroparaffins, when treated with nascent nitrous acid, behave quite differently from the primary compounds. On adding sulphuric acid to the mixed solutions, a deep blue colour is produced and insoluble substances are formed, isomeric with the nitrolic acids, but which have no acid character. They were called by Meyer pseudonitroles, and have been regarded as nitrosonitro-compounds.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}NO\\NO_2\end{matrix}.$$

Their formation may be thus represented

$$(CH_3)_2CH\cdot NO_2 + OH\cdot NO = H_2O + (CH_3)_2C(NO)\cdot NO_2.$$

Scholl subsequently discovered that these substances may be obtained by the action of nitrogen peroxide upon the ketoximes: thus with acetoxime:

$$4(CH_3)_2C{:}N\cdot OH + 3N_2O_4 = 4(CH_3)_2C\!<\!\!\begin{matrix}NO\\NO_2\end{matrix} + 2H_2O + 2NO,$$

a mode of formation which, as Meyer pointed out, indicated that they may be regarded as the nitrates of the oximes, $(CH_3)_2C{:}N\cdot O\cdot NO_2$. Their formation from the secondary nitro-compounds may be supposed to occur in the following phases:

$$(CH_3)_2CH\cdot N\!<\!\!\begin{matrix}O\\O\end{matrix} + HNO_2 = (CH_3)_2CH\cdot N\!<\!\!\begin{matrix}O\cdot NO_2\\OH\end{matrix},$$

$$(CH_3)_2CH\cdot N\!<\!\!\begin{matrix}O\cdot NO_2\\OH\end{matrix} - H_2O = (CH_3)_2C{:}N\cdot O\cdot NO_2.$$

Meyer was inclined to give the preference to the latter view of their constitution, as it is generally very doubtful whether compounds containing a nitroso-group (NO) directly linked to a carbon atom are capable of existence.

Tertiary nitro-compounds are unchanged by the action of nascent nitrous acid.

Meyer pointed out how the characteristic colour reactions afforded by the behaviour of nitrous acid with the primary and secondary nitroparaffins, and its inability to act upon the tertiary compounds, offered a ready means of distinguishing primary, secondary, and tertiary alcohol radicles. The iodide to be tested is distilled with silver nitrite, the distillate shaken with a solution of potassium nitrite in strong potash, diluted with water, and mixed drop by drop with dilute sulphuric acid. If the liquid acquires a red colour (formation of nitrolic acid) which disappears with excess of acid and reappears on the addition of alkali, we are dealing with a primary radicle: should the liquid give a blue colour (formation of pseudonitrole) soluble in chloroform, the compound is derived from a secondary alcohol radicle; the non-formation of colour indicates a tertiary radicle. The test ceases to be of much practical value beyond the 5 carbon series (compare Meyer and Jacobson, *Lehrbuch der Organischen Chemie*, 1893, 253, *et seq.*).

The same line of inquiry was extended to the other main groups of aliphatic substances, and resulted in the discovery of new types of compounds. Thus, by the reduction of the isonitrosoketones and the isonitrosoacetoacetic esters, Meyer, in conjunction with Treadwell, obtained a series of volatile bases having apparently the generic formula $C_nH_{2n-4}N_2$, which they termed ketines and subsequently aldines. This group of substances is now generally known as the azines, and the substance first described by Meyer and Treadwell is dimethylpyrazine,

$$2CH_3\cdot CO\cdot CH{:}N\cdot OH + 6H = N\begin{<}\begin{matrix}C(CH_3){:}CH\\ CH{:}C(CH_3)\end{matrix}\end{>}N + 4H_2O.$$

Meyer had the faculty of keeping more irons hot at a time than any man of his period. Although much of his thought and energy was directed in the first years of his sojourn in Zürich to the development of the new field of inquiry which his discovery of the nitroparaffins opened out, he continued his work on aromatic compounds, partly in defending positions he had already secured, and partly in breaking new ground. In the latter connection, reference may be made to his discovery, with Michler, of diazoxybenzoic acid, and to the new class of azo-compounds which he described in conjunction with Ambühl.

A point of some little interest at the time (1875) was his discovery that hydroxylamine and nitrous acid together yield nitrous oxide and water, $NH_3O + NO_2H = 2H_2O + N_2O$, in the same manner that nitrous acid and ammonia form nitrogen and water. The production of nitrous oxide by mixing together concentrated aqueous solutions of

hydroxylamine sulphate and sodium nitrite constitutes a neat and striking lecture experiment. He also showed, with Locher, that hydroxylamine may be obtained by a number of new reactions, as, for example, by acting on dinitropropane or ethylnitrolic acid with tin and dilute hydrochloric acid, when, in the one case, the amine is liberated in conjunction with acetone, and, in the other, together with acetic acid.

(1) $CH_3 \cdot C(NO_2)_2 \cdot CH_3 + 8H = CH_3 \cdot CO \cdot CH_3 + 2NH_3O + H_2O$.
(2) $CH_3 \cdot C(N \cdot OH) \cdot NO_2 + 4H + H_2O = CH_3 \cdot CO_2H + 2NH_3O$.

These reactions showed that the rule, hitherto regarded as universally true, that nascent hydrogen reduces nitroxyl to amidogen, has its exceptions.

But perhaps the most important of Meyer's discoveries at this period was that of the oximes. He had observed that dibromonitroethane, under the action of hydroxylamine, passes into ethylnitrolic acid, and he anticipated that the analogous nitrosoacetone would be formed in like manner from unsymmetrical dichloracetone. Experiment showed, however, that the chlorine in dichloracetone was replaced by a hydroxylamine rest, whilst the ketonic oxygen was replaced by the oximido-group, forming a compound termed by Meyer acetoximic acid, but now known as methylglyoxime, $CH_3 \cdot C(:N \cdot OH) \cdot CH(:N \cdot OH)$. The fact that hydroxylamine would thus react upon carbonyl oxygen induced him, in conjunction with Janny, to study the action of this reagent upon ordinary ketones and aldehydes, and thus led to the discovery of the ketoximes and the aldoximes. This discovery has a two-fold significance. The reaction not only serves to indicate the existence of carbonyl oxygen in compounds, and hence is of value as a mode of determining constitutional problems, but it brought into existence a number of substances yielding derivatives of considerable interest. Further, it is not too much to say that the stereochemistry of nitrogen takes its rise from the discovery of the oximes.

With Janny, he likewise obtained α-nitrosopropionic acid by the action of hydroxylamine on pyroracemic acid, a reaction which is almost quantitative and capable of being used as a test for pyroracemic acid.

Lossen discovered hydroxylamine as far back as 1865. Although it was quickly recognised as an exceedingly reactive substance, its use was greatly curtailed by the difficulty and expense of preparing it in quantity. Much of it, prior to 1883, was obtained by Dumreicher's process, namely, by reducing ethyl nitrate by means of stannous chloride and hydrochloric acid. Meyer showed how the irksomeness of the method, entailed by the necessity of removing the tin by sulphuretted hydrogen, and of dealing with the large volume of liquid produced,

might be materially lightened, and considerable quantities of hydroxylamine salts were made by the modified process in the Zürich laboratory.

The position which hydroxylamine occupies between ammonia and nitric acid, which at that time were held to be the main nitrogenous foods of plants, as well as its great chemical activity when compared with the inertness of the other substances, seemed to Meyer to point to a possible formation of hydroxylamine within the plant, and to its playing an important part in the assimilation of starch and in the formation of albuminoids. In conjunction with Schulze, he therefore made comparative experiments on the action of hydroxylamine, ammoniacal salts, and nitrates upon plants, when it was quickly found that hydroxylamine acted as a poison to vegetable organisms. Meyer, however, points out that it may still be possible that hydroxylamine may be formed in transition products, and yet act as a poison when taken up by the roots, just as peptone behaves as a poison when injected into the veins of animals.

Reference may here be made to Meyer's attempts to elucidate the constitution of ammonium salts. It was found that the dimethyldiethylammonium iodide, obtained by the action of ethyl iodide on dimethylamine, is identical with that produced by acting with methyl iodide on diethylamine, and no difference can be detected in the character of their salts. As the substances, although identical, were obtained by different reactions, it was inferred that they could not be 'molecular' compounds, that is, combinations of a tertiary base with an alkyl haloid, but must contain pentavalent nitrogen, whence, by analogy, ammonium chloride would be

This assumption is only sound on the supposition that, in the formation of the salts, no change had taken place in the position of the alcohol radicles. The main conclusion would be invalidated if, for example, ethyl iodide, when reacting on trimethylamine, did not combine directly with it but was decomposed, as Lossen had suggested, as follows:

$$N(CH_3)_3 + C_2H_5I = CH_3I + N(CH_3)_2C_2H_5.$$

To ascertain if such an interchange occurred, Meyer, in conjunction with Lecco (*Annalen*, 1876, 180, 173), studied the action of ethyl iodide upon tetramethylammonium iodide. If Lossen's contention were sound, the reaction should be

$$N(CH_3)_4I + C_2H_5I = CH_3I + N(CH_3)_3C_2H_5I.$$

No action, however, was found to occur either with ethyl or methyl iodide alone at any temperature up to 180°, or in presence of methyl alcohol or water. Ladenburg and Struve tested Meyer's conclusion by making similar experiments with benzyl iodide and triethylamine, and with ethyl iodide and benzyldiethylamine, and were disposed to regard the resultant compounds as isomeric, although closely alike in most of their properties. On repeating the observations, Meyer found that no difference existed; the substances prepared in the two ways were absolutely identical.

Suggestive and fruitful in ideas as Meyer was, he was seldom at a loss in devising means to put them to the test of trial. In many of his mental characteristics not unlike Davy, as an experimentalist, he had all Davy's resourcefulness with far more than his patience.

As I knew him in Heidelberg, he was an excellent manipulator; still his temperament would never have permitted him to better the example of the great master under whom he was trained. We could all look on and marvel at the patient, concentrated power with which Bunsen would devise, elaborate, and perfect some new form of apparatus, or some new method of analysis. The first steps were very simple—so simple indeed that it was frequently impossible to divine their ultimate purpose. It was from such small beginnings that we obtained the whole process of gasometric analysis, the burner, the photometer, the various voltaic batteries, the spectroscope, the filter-pump, the ice-calorimeter, the flame reactions, &c. Before Bunsen gave a piece of apparatus to the chemical world, he left it practically perfect; the striving after perfection was a veritable passion with him, and numerous were the forms or modifications through which the apparatus or the method passed before he rested satisfied with it. Although Meyer's genius was of a different order, the influence of the Heidelberg training is to be recognised in the various forms of laboratory apparatus with which his name is connected. Chief among these are his modes of determining vapour densities. The elegant modification of Gay Lussac's method introduced by Hofmann left nothing to be desired in the case of comparatively volatile substances unacted upon by mercury, but many bodies were known, and their number was being rapidly increased, in which this method was inapplicable. Meyer accordingly, in 1876, devised his displacement method (*Ber.*, 1876, 9, 1216). This in principle was similar to the method suggested by W. Marshall Watts as far back as 1867, from which it differed in that Wood's metal—an alloy of bismuth, lead, tin, and cadmium, melting below 70°—replaced the mercury, and that the volatilisation was effected at the temperature of boiling sulphur, that is, at 444°. This process allowed of the determination of the vapour density of many substances which could

be vaporised at temperatures below the boiling point of sulphur, and compounds like diphenyl, methylanthracene, triphenylamine, paradibromobenzene, and paradiphenylbenzene, had their vapour densities ascertained for the first time by means of it.

The method was further modified in the following year (*Ber.*, 1877, 10, 2068), mercury being used instead of Wood's metal and the vapours of boiling water, aniline, ethyl or amyl benzoate or diphenylamine—depending on the temperature required—were employed as a bath instead of sulphur vapour.

The "Luftverdrängung Methode"—the simple and extremely convenient process—which will for all time be associated with the name of Victor Meyer, was devised in 1877 (*Ber.*, 1877, 11, 1867). The apparatus is now one of the commonest articles of laboratory furniture, and it is not too much to say that, thanks to the ease with which the whole operation may be carried out, more vapour densities have been determined by its aid than by any other means.

The apparatus is usually constructed of glass, but by making it of glazed porcelain, determinations can be effected at very high temperatures. Except for special reasons, neither the temperature of the heated bulb nor its volume need be known: all that is required is that the temperature should be sufficiently high to gasify the substance under examination. A variety of liquids—water, xylene, aniline, ethyl benzoate, amyl benzoate, diphenylamine—depending on the temperature needed to effect complete vaporisation, may be used as media for heating the bulb. For temperatures exceeding 300°, a bath of molten lead may be employed, the glass bulb of the apparatus being coated, as suggested by Watson Smith and Davis, with a moderately thick film of soot before immersion in the bath so as to diminish the risk of fracture.

Mr. Watson Smith, who was with Meyer at Zürich, and who has kindly sent me some reminiscences of him at this period, writes: "It was somewhat singular that just as Victor Meyer, with Carl Meyer (no relation), had completed their vapour density apparatus for bodies of very high boiling point, I had just obtained in the pure state specimens of the three isomeric dinaphthyls, all of which urgently awaited the determination of their vapour densities. They were the first new high boiling substances with which the apparatus and method were tried. Victor Meyer was immensely pleased and interested with this circumstance, and we practically all three worked the determination together, the results amply proving the reliability and accuracy of the new method. Of course in these cases the lead bath was used" (compare Trans., 1879, 35, 226; 1880, 37, 491).

The molecular weights of a number of substances were quickly ascertained by this method, for example, phosphorus pentasulphide, indium chloride, cuprous chloride, stannous chloride, arsenious oxide,

antimonous oxide, cadmium bromide, &c. Volatilised in an atmosphere of hydrogen chloride, ferrous chloride yielded values between $FeCl_2$ and Fe_2Cl_4. Ferric chloride at no temperature showed a vapour density corresponding with Fe_2Cl_6, whilst at 750° and 1077°, its molecule would seem to be $FeCl_3$. Potassium iodide at 1320° in an atmosphere of nitrogen had a density corresponding with KI. Arsenic and phosphorus at a white heat had densities approaching the values for As_2 and P_2, whilst zinc at 1400°, and bismuth at 1700°, were found to be monatomic, and thallium at 1700° diatomic.

In 1879, the two Meyers, Victor and Carl, astonished the chemical world by announcing (*Ber.*, 1879, 12, 1426), as the result of determinations of their vapour densities at high temperatures, that the halogens were capable of undergoing dissociation or possibly decomposition. As regards chlorine, this announcement at once threatened to re-open a question which had been regarded by most people as practically settled since July 12th, 1810, when Davy read to the Royal Society his classical memoir on oxymuriatic acid. Davy, it is true, had never stated that chlorine was an element in the absolute sense of that term. What he inferred was that it was a substance which "has not as yet been decompounded," and therefore is "elementary as far as our knowledge extends." The very name chlorine, which he suggested, inculcated this view. "To call a body which is not known to contain oxygen and which cannot contain muriatic acid, oxymuriatic acid, is contrary to the principles of that nomenclature in which it is adopted. . . . After consulting some of the most eminent philosophers in this country, it has been judged most proper to suggest a name founded upon one of its obvious and characteristic properties—its colour, and to call it *chlorine*, or *chloric gas*. Should it hereafter be discovered to be compound, and even to contain oxygen, this name can imply no error, and cannot necessarily require a change."

Had chlorine then been 'decompounded'? Did it contain oxygen? Were Berzelius and Murray right after all? Was there such an entity as murium? The pages of the popular scientific periodicals of the time show how these questions agitated the minds of chemists. The indications of the spectroscope were advanced as confirmatory of Meyer's results, and there was much exercise of 'the intelligent anticipation of events before they occur' which occasioned him some annoyance at the time. However sanguine he might be that he had decomposed chlorine, and however freely he might talk with his colleagues, he never committed himself in print to any statement of the kind. To begin with, the amount of oxygen he had obtained was very small, and there was uncertainty as to the action of the chlorine upon the silica or alumina of the

porcelain at the high temperature, and whether the materials employed were wholly free from moisture. I have it, on the authority of Professor Lunge, whose knowledge was derived from daily intercourse with him, that Meyer himself refused to consider the fact as established until he had worked in an apparatus made of material devoid of oxygen, and to this end he obtained a special grant from the Zürich authorities to defray the cost of a vessel of platinum.

Meanwhile Meyer's observations on chlorine were repeated, and their validity impugned by Crafts (*Compt. rend.*, 1880, 90, 183 *et seq.*) who found, by a modification of Meyer's method, that the gas, even at the highest temperature of the Perrot furnace, showed no change indicative of dissociation or decomposition. Meyer, in conjunction with Züblin, at once repeated Crafts' determinations on pre-formed chlorine and confirmed their accuracy.

As regards bromine and iodine, however, the observers were in substantial agreement.

Thus with iodine :

Victor Meyer.			Crafts and Meier.		
Temp.	Density.	D'/D.	Temp.	Density.	D'/D.
450°	8·85	—	445°	8·74	—
586	8·72	0·99	830—880	8·07	0·92
842	6·76	0·77	1020—1050	7·01	0·80
1030	5·75	0·66	1275	5·82	0·66
1570	5·70	0·65	1390	5·28	0·60

Naumann showed from these results, on the assumption that the molecule I_2 splits up into two atoms $I+I$, that the course of the dissociation is in accordance with the result required by the mechanical theory of gases, namely, that the increments of decomposition corresponding to equal differences of temperature increase gradually from the temperature at which dissociation begins up to that at which 50 per cent. of the vapour is decomposed, and then decrease in a similar manner up to that temperature at which dissociation is complete.

In conjunction with Langer, Meyer greatly extended these observations, and subsequently published them as a monograph, entitled "Pyrochemische Untersuchungen" (Braunschweig: Vieweg u. Sohn, 1885).

As regards bromine, they found that the gas, when sufficiently diluted with air, had a normal density, namely, 5·52 even at the ordinary temperature, and no sensible change occurred up to 900° even when diluted with eleven times its volume of nitrogen. At 1200°, the density had diminished to 4·3 on dilution with five volumes of nitrogen. At a white heat, the density of the diluted bromine fell to 3·6. Experiments at higher temperatures were not possible,

as at above 1600° the platinum apparatus is rapidly attacked by both bromine and chlorine.

The alteration in density of bromine vapour at high temperatures has recently been studied by Dr. Perman and Mr. Atkinson, who have found that no sensible diminution occurs up to about 750° at atmospheric pressure, at which point dissociation becomes just appreciable, especially at low pressures, and gradually increases with increasing temperature (*Proc. Roy. Soc.*, 1900, **66**, 10).

In the case of chlorine, it was found by Meyer and Langer that no analogous change occurred below 1200°, no matter whether pure or highly diluted chlorine was employed. At 1400°, however, the density of the diluted chlorine fell from the normal value 2·45 to 2·02.

Similar observations with carbon monoxide seemed to show that at 1690° this gas is partially decomposed into carbon dioxide and carbon, $2CO = C + CO_2$. Carbon dioxide itself experiences no change in density at this temperature in a platinum apparatus, although when passed through a porcelain tube filled with broken pieces of porcelain it undergoes dissociation, as already shown by Deville. This phenomenon may be connected with the remarkable observation of Menschutkin and Konowaloff that dissociable vapours are far more rapidly broken up in presence of asbestos, or pieces of glass, or even of the roughened sides of glass, than when the interior of the glass vessel is perfectly smooth.

Nitrous oxide, heated in a porcelain tube, is entirely resolved into oxygen and nitrogen at 900°, and in a platinum tube at 1690°. Nitric oxide remains unchanged up to 1200°; at 1690°, it is completely decomposed into its elements. Hydrogen chloride also appears to be partially, whilst sulphuretted hydrogen is entirely, decomposed at the latter temperature. Cyanogen has a normal density up to 800°; at 1200°, it suffers decomposition.

Meyer made his pyrochemical investigations under very unfavourable conditions. The magnificent chemical institution which Zürich now possesses was not then built. The old laboratory was a low building to the east of the main block of the Polytechnicum, and the only room which could be spared for the purpose was so small that, in spite of the best ventilation possible, the temperature not unfrequently rose to 50°. Moreover, both he and his assistants suffered greatly from the strenuous ardour with which the work was carried on, and he himself eventually broke down under the strain of it. I saw him in Zürich in the autumn of this year (1879), and was surprised and shocked to notice, although it was at the end of the vacation, how nervous and jaded he seemed. I believe the distressing insomnia from which he suffered at times throughout the rest of his life began at about this period. In reference to this time, Mr. Watson Smith writes: "Meyer had a most excitable

mind and was a tremendous worker. His assistant, Carl Meyer, told me that on several occasions he was so overworked, not by compulsion, but through the mere influence of Meyer's presence, his mental power, and enthusiasm, that he came very near committing suicide during the fits of depression following exhaustion after long-continued spells of work."

Pyrochemical problems continued to interest Meyer to the end, and he was quick to take advantage of any hint which seemed to promise the possibility of their solution. In a lecture before the Naturforscher Versammlung in Heidelberg, he regretted that the lack of vessels of sufficiently refractory material prevented him from working at the higher limits of temperature even then attainable. "There can be no doubt," he said, "that new and undreamt-of discoveries will manifest themselves—that a new chemistry will disclose itself, when we are furnished with vessels that will enable us to work at temperatures at which water can no longer exist, and at which oxy-hydrogen gas becomes an uninflammable mixture."

Shortly before his death, he returned to the subject with new apparatus made of a platinum-iridium alloy capable of withstanding a far higher temperature than pure platinum, and he was in hopes of being able to construct vessels of magnesia which would allow of the application of temperatures over 2000°.

Meyer, at the time he announced his discovery of the dissociation of the halogens, was thirty-one years of age. He was now on the flood-tide of his prosperity. His published work had shown him to be an investigator of uncommon power and originality, and students flocked to him from all parts, to participate in the pioneering work which his astonishing energy and enthusiasm opened out. In its triumphs it was indeed a time of "joyous yesterdays and confident to-morrows." He was happily married to the friend of his youth, Fraülein Hedwig Davidson, whose 'Verlobungstag' was the very day on which he received his call to Zürich. What she was to Meyer only those who were privileged to know his home circle can fully realise.

Meyer's first great grief came to him with the death of his eldest daughter, and in 1882 he lost his friend Wilhelm Weith, Professor of Chemistry in the University. How close and intimate was their friendship was evident to all who frequented the meetings of the Zürich Chemische Gesellschaft, where the two professors were generally to be found seated side by side at the head of the table; it is reflected too in the obituary notice of his colleague which Meyer wrote for the *Berichte*.

In the autumn of 1882, Meyer was requested to undertake the delivery of the series of University lectures on benzene derivatives

which had been interrupted by Weith's death. I have already attempted to indicate what Meyer was as a teacher. No one could possibly take greater pains in the preparation of his lectures, or study more to make them instructive and interesting. It is generally supposed that organic chemistry does not lend itself to effective lecture illustration. Such was not the case when Meyer had to teach it. "I well recollect," writes Mr. Watson Smith, "that the word most frequently used in Zürich in defining the opinions of Victor Meyer's students of his lectures was 'brilliant!'" Another of our Fellows, Mr. John I. Watts, who attended his course in 1879-80, writes:—

"What particularly struck me about his lectures was their finished style. He made fairly constant use of notes, speaking with great rapidity. Yet his treatment of the subject was very clear, and his language perfect. The experiments were always well prepared and exceptionally successful. Indeed, his lectures were most popular, and both at his work and outside the Polytechnic there was no professor who was more respected and admired by all students than Victor Meyer. Young, handsome, well-dressed—for a German professor, with a quick wit and a genial manner, he was a welcome addition to any gathering. When, in 1881, he had a 'call' to Aachen and elected to remain at Zürich, the students treated him to a torchlight procession and a grand 'Kommers.' Meyer watched the 'Fackelzug' of over 1000 students from a balcony, and later, sitting as the honoured guest in a still greater throng, he seemed indeed a happy man."

Similar testimony is given by Dr. Sudborough, who was with him in Heidelberg, and who writes:—

"As a lecturer, Meyer was clear, concise, and extremely lucid, and his delivery was easy and natural. His lectures were given by the aid of carefully written notes, and were fully illustrated by experiments, the table being always crowded with apparatus both in the organic and inorganic lectures. It was very rare indeed for an experiment to fail; this was firstly due to Meyer's own dexterity as a manipulator, and also to the care which was bestowed upon the preparation of the experiments."

It was in the course of these lectures on benzene derivatives that Meyer came upon what is perhaps the most brilliant of all his discoveries—that of thiophen. How he lighted upon it is well known, but the story bears repetition. He desired to show his class the so-called indophenin reaction of Baeyer, at that time held to be indicative of benzene, but to his astonishment not a trace of the characteristic blue colour made its appearance, although, as was his wont, he had rehearsed the experiment just prior to the lecture. It appeared that his assistant, Sandmeyer—himself one of Meyer's 'discoveries'—had handed to him a sample of the benzene made in the lecture course by heating benzoic acid with lime, and at once drew his attention to the fact that the rehearsal had been made with the ordinary laboratory supply—

the *Benzol purissim. crystallisatum* of the dealers, and, of course, derived from coal-tar. Meyer, at the moment, was so fully occupied that he might well have put aside the incident, or have given no immediate heed to its significance. But that was not his way. Fortune scatters her chances indifferently, and every man may have his share, but it is not given to each to perceive when he is favoured, or to know when to grasp "the skirts of happy chance." Madame de Staël once said that a most interesting book might be written on the important consequences which spring from little differences, and it was the little difference that riveted itself on Meyer's mind. He at once began the investigation of the cause. All kinds of benzene to be found in Zürich were tested, and it was soon definitely established that it was only coal-tar benzene that gave the indophenin reaction. Meyer's first idea was that it might be occasioned by an isomeric—a second benzene found in coal-tar. Within less than a month he had ascertained that the reaction was due to some sulphuretted product accompanying coal-tar benzene, and that Baeyer's indophenin was probably a sulphur compound. Meyer's action was characteristic of him. Before communicating with Baeyer, he carefully repeated his experiments, and only when all ground for doubt was removed did he inform his friend of his observations and of the inferences he had formed. Baeyer at once sent him a specimen of his indophenin, and the fact that it actually was a sulphuretted compound was then established. Meyer found that coal-tar benzene, after repeated shaking with oil of vitriol, no longer reacted with isatin, and hence he determined to search among the sulphonic acids so formed for the reactive substance. By distilling the product obtained by shaking 10 litres of benzene with oil of vitriol, he obtained a few cubic centimetres of a clear, thin, mobile liquid containing sulphur, which boiled at about 83° and remained liquid in a freezing mixture of ice and salt. It gave a most intense reaction for indophenin. The amount of the new substance present in coal-tar benzene was very small, at most not more than 0·5 per cent.

Thanks to the co-operation of his friends, Messrs. Bindschedler, Busch and Co., of Basle, he was enabled to repeat this experiment on a large scale, as much as 250 litres of coal-tar benzene being operated upon at a time, and the sulphonic acids converted into the lead salts, which were then mixed with sal ammoniac and distilled. The crude product, which contained about 28 per cent. of sulphur, was found to react strongly with bromine, forming a heavy, colourless, highly refractive liquid, boiling at 211°, greatly resembling dibromobenzene, but showing on analysis the composition $C_4H_2Br_2S$. The new compound was the dibromo-substitution product of a substance which

Meyer was at first inclined to call *thianthren*, then *thiophan*, next *thiol*, and lastly *thiophen*, to denote that it was a sulphur-containing substance giving derivatives analogous to those of phenyl.

In the early part of the following June, that is, within about six months of his first observation, he had obtained a considerable quantity of thiophen, and was in a position to show to the Swiss Naturforscher Versammlung, which met during that summer in Zürich, that its chemistry was hardly less extensive than that of benzene itself. Thus it was that a chance observation—the observation of a little difference—added a new section to organic chemistry.

It would be quite impossible within the limits at my disposal to show how this section was developed by Meyer and his pupils. In 1888, he published, in the form of a monograph, dedicated to his friend and patron, President Kappeler, "dem hochherzigen Förderer wissenschaftlicher Bestrebungen," an account of its condition at that time (Die Thiophengruppe. Braunschweig: Vieweg u. Sohn), from which it appears that during the preceding five years no fewer than 106 contributions to its history had been made from his own laboratory, and some 40 from those of others. How fertile the field still continues may be gleaned from the circumstance that upwards of 50 papers on the same subject have since made their appearance in various journals.

Meyer's restless energy had now begun to react most seriously upon his general health. At times he was almost prostrated by nervous exhaustion; he had frequent spells of insomnia, and his friends viewed with alarm the signs of physical decay which now set in, in spite of the occasional holidays, mainly among the Alps, which he gave himself. In 1884, he again broke down, and although at the moment he was immersed, with his colleague Lunge, in the plans for the new chemical laboratory of the Polytechnic in which, as he states, he had hoped ultimately to resume his pyrochemical labours under more favourable conditions, he was obliged to relinquish, for a time, all idea of work, and towards the end of the year was ordered away to the Riviera, where he wintered. In the following spring, he received a 'call' to Göttingen as the successor of Hübner. This he eventually decided to accept, and entered upon his duties there in the summer session of 1885.

He was not able, as he had hoped, to take leave of his Zürich students at the time, but what they thought of him—with what affection and respect he was regarded—was seen in the terms of the Address they sent to him on the occasion of his opening lecture at Göttingen. It was seen, too, in the way he was received by them during a visit to Zürich some months later, on the occasion of the seventieth birthday of his friend Kappeler. Professor Goldschmidt,

who was present, thus describes the scene: "I see him even now before me as he spoke to the students at the 'Kommers' in the evening. The 'Zürcher Polytechnikers' have, as a rule, but little opportunity of knowing the professors outside their special faculty, and have, therefore, but little interest in those who are not their own teachers. As Victor Meyer's slender form appeared on the platform, and as his bright blue eyes glanced round the assembly, there broke forth a shout of welcome from all—engineers, machinists, architects, as well as from his old students the chemists—to be ended in a whirlwind of applause at the close of a speech, sparkling and witty as ever."

With renewed health and vigour, he now set about the plans for the new laboratory which the authorities had decreed should adorn the 'Georgia-Augusta,' for Wöhler's old place no longer sufficed to contain the chemical workers which Göttingen had now to receive. Whilst it was being erected, he continued his pyrochemical work, and his investigation of the thiophen derivatives, and began with Paul Jacobson the admirable "Text-book of Organic Chemistry," which, in the critical selection and arrangement of its material, is still unsurpassed.

With Auwers, he resumed the study of benzil and its derivatives which he had begun with Wittenberg and Goldschmidt. With Münchmeyer, he began the study of the behaviour of phenylhydrazine towards various groups of oxygen compounds, and he sent a short paper to the *Berichte* on thiodiglycol compounds, and on an easy method of preparing β-iodopropionic acid from glycerol. With Demuth, he undertook the investigation of the sulphuranes, a group of disulphides of the general formula $C_2H_3 \cdot S \cdot C_2H_4 \cdot SR$. Other papers were on the density of nitric oxide, which showed no evidence of association or molecular duplication even at $-100°$; on isophthalaldehyde; on the negative nature of the phenyl group; and on isodibromosuccinic acid.

It was characteristic of his receptivity that Meyer should be among the earliest workers in Germany to perceive the value of Raoult's method of ascertaining molecular weights; it was first used in the Göttingen laboratory to determine the molecular weight of some derivatives of benzil which yielded two series of isomeric compounds, both series having the same constitution, in the ordinary sense, but which were yet distinct from one another and yielded different derivatives.

Other papers of this period were on the thio-derivatives of deoxybenzoin and its analogues (desaurins), and, with Riecke, on the carbon atom and valency. The latter paper is of interest as an example of Meyer's "scientific use of the imagination," and may

be studied in connection with an earlier paper in 1876 (*Annalen*, 1876, 180, 192) on the same subject, as showing how he grafted the theoretical conceptions of van't Hoff upon the teaching of Kekulé. According to Meyer, the carbon atom is surrounded by an ethereal shell which, in the case of an isolated atom, has a spherical form; the atom itself is the carrier of the specific affinities, the surface of the shell is the seat of the valencies; each affinity is determined by the existence of two opposite electrical poles, which are situated at the end-points of a straight line small in comparison with the diameter of the ethereal shell. Such a system of two electric poles is called a double- or di-pole. The four valencies of a carbon atom would be represented by four such di-poles, the middle points of which are situated on the surface of the ethereal shell, but freely movable within it. The di-poles themselves can rotate freely round their middle point. The carbon atom has a greater attraction for positive than for negative electricity, and the positive pole of a valency is slightly stronger than the negative pole. This hypothesis explains why the four valencies take up the position of a regular tetrahedron; why they can be diverted from this position; why the valencies of one and the same carbon atom cannot combine together, whilst the valencies of different carbon atoms can do so; why there are two kinds of single-binding, one stable, and the other allowing free rotation; and lastly, why free rotation ceases in cases of double- or treble-binding (*Ber.*, 1888, 21, 946; compare Abstr., 1888, 549).

Stereochemical questions—we owe the phrase to Meyer—were indeed at this time occupying much of his thought. In a paper with Auwers (*Ber.*, 1888, 21, 784), he pointed out that the existence of the two isomeric dioximes of benzil, discovered by him in conjunction with Goldschmidt, would, if for both the formula

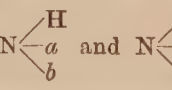
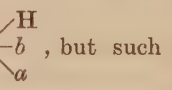
$$C_6H_5\cdot C(N\cdot OH)\cdot C(N\cdot OH)\cdot C_6H_5$$

were established, be in direct contradiction to the hypothesis of van't Hoff that two carbon atoms united by a single affinity are free to rotate, the axis of rotation being the bond of union, and that isomerism is only possible for those substances of the type $\equiv C—C\equiv$, which cannot, by rotation round the common axis, be converted into the same form. The two dioximes were carefully compared as regards their melting points, solubilities in water, alcohol, ether, or acetic acid, and the conditions under which the α-form is converted into the β-modification were ascertained. To further remove all doubt as to the possibility of merely physical isomerism, and to prove that the oximes are not only different from one another, but yield different derivatives reconvertible into their respective oximes, the propionic and isobutyric derivatives were prepared and compared. The result showed that the dioximes were of identical chemical composition, and

hence it appeared that van't Hoff's hypothesis must be so altered as to admit of cases in which free rotation round the axis cannot take place, as otherwise no explanation of the isomerism of the α- and β-dioximes is possible (compare Abstr., 1888, 597).

He subsequently showed how the work of Bethmann, Graebe, and Baeyer confirmed these views. Wislicenus' theory as to the free rotation of singly-bound carbon atoms would appear to be limited to certain cases; absolutely free rotation is probably possible only when the substituting atoms or groups are identical; where, as is the case in the majority of compounds, the atoms or groups are not identical, there will be some definite position of equilibrium; only in cases where the substituting atoms or groups are equally negative will there be several positions of equilibrium (*Ber.*, 1890, 23, 2079; Abstr., 1890, 1083).

Meyer's perspicacity and critical insight are well illustrated in a lecture which he gave to the German Chemical Society in 1890 "On the Results and Aims of Stereochemical Research." It is of interest to the student as giving a fairly complete historical account of the development of space formulæ, and more especially for its criticism of the work of Baeyer and Wislicenus on the stereochemical formulæ of single-, double-, and treble-linked carbon compounds, and of the stereochemical conceptions of Hantzsch and Werner in the case of nitrogen compounds.

With regard to the assumption that the nitrogen atom may be represented as a tetrahedron, and that the isomerism of the benzaldoximes may be similar to that of fumaric and maleic acids, it is pointed out that the structure of the oximes is in all probability not identical. Two isomeric forms of each of the unsymmetrical oximes of the formula OH—N:CXY are indicated by the hypothesis of Hantzsch and Werner, but they do not appear to exist. If the tetrahedral representation of the nitrogen atom were tenable, we should have to assume that substituted ammonias can exist in the isomeric forms  and  , but such bodies are not known. We must therefore assume that in ammonia the hydrogen atoms are placed symmetrically with regard to the nitrogen atom, and this can only find expression in a plane formula (*Ber.*, 1890, 23, 567; compare Abstr., 1890, 719).

Reference may be made here to the short paper on isomeric oximes of unsymmetrical ketones and the configuration of hydroxylamine, in conjunction with Auwers (*Ber.*, 1890, 23, 2403), in which the authors advance further evidence that the isomerism of the oximes cannot depend upon structural dissimilarity, but must be sought for in the

nature of the hydroxylamine group. Assuming the correctness of the theories of van't Hoff and Wislicenus regarding the arrangement of atoms in space, the combined effect of the attraction of the nitrogen and oxygen on the hydroxylic hydrogen of hydroxylamine would cause it to be in a plane different from that occupied by the remaining atoms in the molecule. This hypothesis suffices to explain all observed facts: unsymmetrical oximes would therefore exist in two forms, $\overset{a}{\underset{b}{C}}\!:\!N\cdot\overset{H}{O}$ and $\overset{a}{\underset{b}{C}}\!:\!N\cdot\underset{H}{O}$. The difference between this theory and that of Hantzsch and Werner is shown by the two formulæ,

$$\overset{OH}{C}\!:\!N \qquad \text{and} \qquad \overset{H}{C}\!:\!N\!-\!O\ .$$

(Hantzsch and Werner). (Auwers and Meyer).

The formation of an oxime by the action of nitrous acid is readily accounted for on the ground that it is a substituted hydroxylamine; moreover, the fact that no case of geometrical isomerism has ever been observed in the azo-, azoxy-, and imido-compounds tells in favour of this theory (compare Abstr., 1890, 1263).

To this period belongs also the work on the azines; on deoxybenzoin; on the aromatic nitriles; on tetramethylsuccinic acid; and on the oximes of phenanthraquinone.

Meyer was not destined to remain long in Göttingen. The new laboratory was barely finished, when, in 1889, he received a 'call' to Heidelberg. Bunsen, full of years as of honours—the Nestor of Chemistry, as his friends were wont to call him—had expressed a wish to retire, and of all his many students there was none, he said, whom he wished more to take his place than he who, twenty-one years before, had worked with him in the modest little room of some four or five places, which had constituted his private laboratory. To Heidelberg accordingly Meyer went, with the coveted title of Geheimrath, and the promise of a new and enlarged laboratory. Although only forty years of age, he was now, so far as worldly position was concerned, at the summit of his career; he had returned to his Alma Mater and the rest of his days were to be given to her service.

During his four years' stay in Göttingen he had in great measure recovered his health and with it the elasticity of his active, buoyant temperament. I saw him in Heidelberg in the spring of 1891, when he was busy with the enlargement of the old laboratory, and it was

with a glance of pride—a pardonable pride—that he pointed out the places where he and I had worked with 'Papa' Bunsen,

'So kindly modest, all accomplished, wise,'

in the corner place near the window, towering above both of us. It was strange, too, to hear the sound of children's voices and their laughter; and the bustle of servants in what were formerly the silent, half-deserted rooms overlooking the Wrede-platz; and stranger still to me was it, as we together called upon Bunsen, sitting solitarily in his rooms overlooking the Bunsen-strasse, to behold the meeting and to listen to the greeting of these two men—the memory of whose names and fame Heidelberg will cherish so long as Heidelberg exists. To all of us life has its dramas, and in some of these the incidents are as moving as those ever conjured up by playwright or poet.

This was the last occasion on which I saw Meyer. How well I remember it! He was as bright, as active, as mentally vigorous as of old, although it was but too obvious that his physical strength was not the equal of his nervous energy.

Meyer's earliest experimental work at Heidelberg was mainly concerned with the continuation of investigations begun at Göttingen. But he was perpetually breaking new ground or seeking to clear up doubtful points in ground already partially explored.

The classical labours of Frankland on zinc ethyl might be thought to have definitely established the chemistry of that substance, but even on such a comparatively simple matter as the action of oxygen on zinc ethyl there was room for still further inquiry. The white compound obtained by Frankland, as the result of the oxidation of zinc ethyl, was regarded by him as a mixture of zinc oxide, ethoxide, and acetate. It was found, however, by Meyer and Demuth to contain no acetate, but to be mainly composed of a peroxide, $ZnEt{\cdot}O{\cdot}OEt$, as proved by its power of liberating iodine from potassium iodide. The explosive character of the substance is thus explained. Zinc ethoxide, in fact, does not appear to have been prepared (*Ber.*, 1890, 23, 394).

In conjunction with a number of his pupils—Krause, Freyer, Askenasy, and others—Meyer in 1891 began the investigation of a subject already associated with the name of his predecessor, namely, on the conditions determining both the gradual and the explosive combustion of gaseous mixtures. Although a considerable amount of experimental work was done, the results obtained, curious and interesting as they were in some particulars, led to no very definite general conclusions.

It was found that the temperature at which combination occurred

varied with the nature of the vessel, and depended upon whether the gases were confined or not. Ignition takes place at a lower temperature when the mixture is in a closed vessel than when passing freely through an open tube. If, however, an open vessel containing the mixture is heated suddenly, explosion takes place at the lower temperature. In the cases of gradual union, no relation between time and amount of combination could be perceived. As showing the influence of the nature of the surface, it was found that, when the bulbs were silvered inside, the union of oxygen and hydrogen was rapidly effected at a temperature of about 200°, whereas in an unsilvered bulb the gaseous mixture had to be heated to above 530° before any sensible amount of water was produced. The principal quantitative results are embodied in the following table in which the mixture did not explode at the lower temperature in each column, but did so at the higher:

Equivalent mixtures.	Free current.	Closed bulbs.
Hydrogen, oxygen	650—730°	530—606°
Methane, oxygen	650—730	606—650
Ethane, oxygen	606—650	530—606
Ethylene, oxygen	606—650	530—606
Carbon monoxide, oxygen	650—730	650—730
Hydrogen sulphide, oxygen	315—320	250—270
Hydrogen, chlorine	430—440	240—270

In a subsequent paper with Münch (*Ber.*, 1893, **26**, 2421), the temperatures of explosion of gaseous mixtures were determined by placing the vessel containing the gases inside the bulb of an air thermometer immersed in a metal bath. The mixture of a gas with the amount of oxygen theoretically necessary for its complete combustion was passed through a fine tube to the bottom of the internal vessel, and lighted as it issued from the mouth of the exit tube. At a certain temperature, the flame ran down the tube and the contents of the vessel exploded. This temperature—the temperature of explosion—was determined by displacing the air contained in the air thermometer by means of hydrogen chloride, collecting it over water, and measuring it. In 38 experiments with a mixture of hydrogen and oxygen (pure electrolytic gas), the temperature of explosion varied from 620° to 680°, being about 650° in mean. The temperature is not affected by variations in the rapidity with which the gaseous mixture enters the glass vessel, or by the presence of fragments of glass or sand. In presence of platinum, the gases combine quietly, and if the glass vessel is very small no explosion occurs.

The temperatures of explosion of a number of aliphatic hydro-

carbons, mixed with equivalent amounts of oxygen, were then determined as follows:

Methane	656—678°	Propane	545—548
Ethane	605—622	Propylene ...	497—511
Ethylene	577—590	*iso*Butane ...	545—550
Acetylene ...	509—515	*iso*Butylene...	537—548

Coal-gas with 3 times its volume of oxygen ... 647—649

It would thus appear that the temperature of explosion falls as the number of the carbon atoms in the molecule increases; that it is probably lower for primary than for corresponding secondary hydrocarbons; and is less for hydrocarbons containing a double bond than for those containing only single bonds, and still less for those containing a triple bond (compare Abstr., 1894, ii, 11).

Mention may here be made of the work done, in conjunction with Bodenstein, on the decomposition of gaseous hydrogen iodide by heat. This gas was selected for the reason that the action of heat upon it is reversible, and hence it might be expected that the establishment of a condition of equilibrium will be in no way influenced by the many disturbing circumstances which were found to occur in the case of other gaseous mixtures.

Combination of hydrogen and iodine vapour takes place even at 444° (b. p. of sulphur), and the hydrogen iodide formed is far more stable, at all events in the dark, than has hitherto been supposed. It is, however, very sensitive to light. In bulbs which were exposed for 10 days to direct sunshine, 58 per cent. of the gas was decomposed, and when exposed throughout the summer, practically the whole of the gas is resolved into its constituents. Experiments on the relation of the amount of decomposition to temperature gave the following results:

		Relative amount of HI decomposed, as determined	
Temperature of boiling		By decomposition.	By direct union.
Sulphur	444°	0·2150	0·2104
Retene	394	0·1957	—
Mercury	350	0·1731	0·1738

At 310° (b. p. of diphenylamine) the relative amount of HI decomposed was 0·1669, instead of 0·1550 as calculated from the above numbers. The difference between the observed and calculated results is due to the circumstance that the heat of formation of hydrogen iodide is, at ordinary temperatures, negative ($-1600°$, Thomsen), but from the fact that the decomposition at temperatures such as 350—444° increases with rising temperatures, it follows from van't Hoff's principle (*Principe de l'equilibre mobile*) that the heat of formation at these

temperatures is positive. There must, therefore, be a temperature at which the heat of formation is zero, and at which also the decomposition is at a minimum. This point, as the experiments show, lies between 310° and 350°, and calculation by van't Hoff's formula showed that it is at 324°. As it was found that two bulbs heated under the same conditions always gave the same result, it was possible to study the decomposition as a time reaction, and by the formula given by Nernst. The constancy in the values actually obtained for each of the foregoing temperatures showed that, in the case of the decomposition of hydrogen iodide by heat, the change occurs in a perfectly regular manner (*Ber.*, 1893, 26, 1146; compare Abstr., 1893, ii, 369).

This short account of Meyer's labours in physical chemistry may conclude with a brief reference to the determinations of the fusing points of salts melting only at relatively high temperatures, which he made in concert with his pupils. These he was able to obtain by the aid of the platinum air-thermometer he described in conjunction with Freyer. The following is a list of his final values:

Sodium chloride.....	815°	Sodium biborate.....	878°
Sodium bromide.....	757	Sodium sulphate.....	863
Sodium iodide	661	Potassium sulphate	1078
Potassium chloride...	800	Cæsium iodide	621
Potassium bromide...	722	Calcium chloride ...	806
Potassium iodide ...	684	Strontium chloride...	832
Potassium carbonate	878	Barium chloride.....	921
Sodium carbonate ...	849	Rubidium iodide ...	641

(Compare Heycock and Neville, Trans., 1895, 67, 190).

In 1892, Meyer and Wachter made known the possibility of the existence of a class of aromatic derivatives, known as the iodoso-compounds, in which the monovalent group IO replaces hydrogen. The first representative of the series was iodosobenzoic acid, $C_7H_5IO_3$, which they obtained by the action of fuming nitric acid or a boiling and acidified solution of potassium permanganate upon orthoiodobenzoic acid. It is a crystalline, solid substance, melting at about 200°, sparingly soluble in water or ether. It liberates iodine from potassium iodide, and chlorine from hydrochloric acid, forming orthoiodobenzoic acid. It is an extremely feeble acid, and its silver salt when dry is highly explosive.

No iodoso-derivatives could be obtained from meta- or para-iodobenzoic acids. Of the two iodoparatoluic acids, the one in which the iodine atom occupies the ortho-position to the carboxyl group yields an iodoso-derivative similar to iodosobenzoic acid, but the

isomeric acid does not yield a corresponding compound. If, however, paraiodobenzoic acid be previously nitrated, it may be converted by the further action of fuming nitric acid into an iodoso-derivative, $IO\cdot C_6H_3(NO_2)\cdot CO_2H$. In like manner, the iodoparatoluic acid may be made to yield an iodoso-compound by previous nitration (*Ber.*, 1893, 26, 1354).

By the further action of oxygen on an alkaline solution of iodosobenzoic acid, iodoxybenzoic acid, $IO_2\cdot C_6H_4\cdot CO_2H$, is formed, a white, crystalline substance, turning red on exposure to light, and decomposing with explosion at 233°. It is a much stronger acid than the iodoso-derivative, forms moderately stable salts, and gives characteristic colour reactions with aniline and phenol (*Ber.*, 1893, 26, 1727; compare Abstr., 1893, i, 577).

Hartmann and Meyer found that when iodosobenzene, $C_6H_5\cdot IO$, is dissolved in strong sulphuric acid, the solution, on dilution with water, yields the sulphate of a base, phenyliodophenyliodonium hydroxide,

$$\begin{matrix} C_6H_5 \\ I\cdot C_6H_4 \end{matrix}\!\!>\!I\cdot OH.$$

A similar change occurs with paraiodosotoluene. The free bases have a strong alkaline reaction, and form characteristic crystalline salts.

Meyer was thus led to the discovery of a remarkable group of substances known as the iodonium compounds, the simplest aromatic representative of which is diphenyliodonium hydroxide,

$$I\begin{matrix} C_6H_5\cdot \\ -C_6H_5\cdot \\ OH. \end{matrix}$$

These bases are compounds in which two of the valencies of the iodine atom are satisfied by aromatic radicles whilst the third is satisfied in the free base by hydroxyl, and in the salts by an acid radicle. The iodonium bases are readily soluble in water, are strongly alkaline, and in their behaviour, as in that of their salts, show a remarkable similarity with the derivatives of silver, lead, and, more particularly, thallium. These bases are formed by the decomposition of the iodoso- and iodo-hydrocarbons under various conditions; for example, by the action of moist silver oxide upon an intimate mixture of equivalent proportions of iodosobenzene and iodoxybenzene,

$$C_6H_5\cdot IO + IO_2\cdot C_6H_5 + AgOH = C_6H_5\cdot I\!<\!\begin{matrix} OH \\ C_6H_5 \end{matrix} + AgIO_3.$$

By the addition of potassium iodide to the aqueous solution, diphenyliodonium iodide is precipitated. This compound stands in the same relation to iodobenzene that trimethylsulphonium iodide does to

methyl sulphide, and as tetramethylammonium iodide does to trimethylamine. It crystallises from alcohol in long, pale yellow needles, and decomposes on heating almost quantitatively into iodobenzene,

$$C_{12}H_{10}I_2 = 2C_6H_5I.$$

If the decomposition is started at one point, it proceeds through the whole mass with development of heat.

The existence of these remarkable bases and salts, which recall the sulphonium-, ammonium-, arsonium-compounds, &c., shows that a complex which is composed of one iodine atom and two molecules of phenyl, that is, of constituents which are otherwise negative, possesses strongly basic properties. From the general behaviour of the iodonium compounds, it is evident that the complex $-I<^{C_6H_5}_{C_6H_5}$ or in general $-I<^{R}_{R_1}$ (where R and R_1 are aromatic radicles) possesses the function of a metal analogous to thallium (compare *Lehrbuch der Organischen Chemie*, Meyer and Jacobson, 2, 127).

It is interesting to note that the physiological action of the diphenyliodonium chloride resembles that of ammonium salts on the one hand, and of heavy metals, such as lead and thallium, on the other. Doses of 0·02—0·03 gram produce total paralysis in frogs, both the motor nerve-ending and the muscle substance being affected. A dose of 0·08 per kilo. proves fatal to rabbits, the spinal chord and *medulla oblongata* being also affected.

A study of the conditions determining the formation and hydrolysis of ethereal salts of aromatic acids occupied Meyer, in conjunction with his pupils, and more especially Sudborough, from 1894 up to the year of his death. It was found that benzoic acid and its substituted products, as a rule, readily yield practically the theoretical quantity of an ethereal salt when treated with methyl alcohol and hydrochloric acid in the cold. On the other hand, the symmetrical trisubstitution products of benzoic acid yield no ethereal salts whatever under these conditions. This rule holds absolutely for all 1 : 3 : 5-trisubstitution derivatives of benzoic acid (Me, NO_2, Cl, Br, I, and CO_2H), except those containing one or more hydroxyl groups. The same is true of all substituted benzoic acids in which the 2 : 6-hydrogen atoms ($CO_2H = 1$) have been replaced by other atoms or groups.

The acids which do not yield ethereal salts when treated with alcohol and hydrochloric acid can readily be converted into these substances by the action of methyl iodide on their silver salts, or of methyl alcohol on the acid chlorides.

This remarkable difference in behaviour may be ascribed to a stereochemical cause, the substituent groups being supposed to hinder the

introduction of the alkyl group to such an extent that under the prescribed conditions the reaction does not proceed.* Acids in which the carboxyl group is linked with the benzene nucleus by one or more carbon atoms readily undergo etherification. The constitution of a substituted benzoic acid may, therefore, be ascertained in this way, and the method may also be used for isolating or purifying those acids which will not undergo etherification.

The nitrophthalic acids behave similarly: dinitrophthalic acid [$NO_2 : CO_2H : CO_2H : NO_2 = 1 : 2 : 3 : 4$] gives no ethereal salt, whilst the acid [$NO_2 : CO_2H : CO_2H : NO_2 = 1 : 3 : 4 : 5$] yields monalkyl salts. 1 : 2 : 6-Dinitrobenzoic acid gives no ethereal salt (Abstr., 1895, i, 93). Chloronitrobenzoic acid [$CO_2H : NO_2 : Cl = 1 : 2 : 6$] yields no ethereal salt, showing that the rule applies when the substituents are dissimilar. Diortho-substituted benzoic acids are not etherified at low temperatures when one of the substituents is hydroxyl.

Meyer was of opinion that etherification, in the case of analogous compounds, is diversely influenced by substituents of different relative mass. He imagined that those radicles which prevent etherification at high temperatures have a much greater relative mass than those which only hinder it at low temperatures, but it is probable that the methyl group and its normal homologues will produce almost identical effects, since the action is chiefly due to that carbon atom which is directly linked to the benzene nucleus. According to theory, those ethereal salts which are formed with greatest difficulty should be hydrolysed least readily, and such Meyer found to be generally the case.†

These conclusions have been tested by Kellas (*Zeit. phys. Chem.*, 1897, **24**, 221), who has measured the velocity of etherification for a large number of monosubstitution derivatives of benzoic acid. From a study of the influence of temperature, and of the nature of the substituent, he has more precisely indicated the limits within which they may be regarded as generally true.

Considerations of space preclude more than a bare reference to the work on the derivatives of ethyl dinitrophenylacetate; on the indoxazen group; on the laws of substitution in the aliphatic series; on the synthesis of triphenylacrylonitrile and on the isomerides of triphenylacrylic acid; on the modes of introduction of acetyl groups into aromatic hydrocarbons; on the substitution of the hydrogen

* This supposition has been modified by Wegscheider, who introduces Henry's conception of the formation of an additive compound between the alcohol and the acid. According to Wegscheider, the ortho-substituents prevent the formation of such additive compounds (compare, however, Davis, Trans., 1900, **77**, 33).

† This is approximately true for the benzoic series of acids, but does not obtain for the acetic and probably other series (compare Sudborough and Lloyd, Trans., 1899, **75**, 467).

in trinitrobenzene by alkaline metals; on the fusibility of platinum; on the formation of tetriodoethylene from diiodoacetylene; on the durenecarboxylic acids; on the action of potassium permanganate on hydrogen, methane, and carbon monoxide; on the slow oxidation of hydrogen and carbon; on the evolution of oxygen during reduction; on hexahydrobenzophenone and its oximes; and on diphenylamine from orthobromobenzoic acid.

Meyer contributed to the literature of chemistry, either alone or in conjunction with his pupils, upwards of 300 memoirs and papers.

No account of Meyer's scientific activity would be complete without some allusion to the various pieces of apparatus with which he enriched operative chemistry. Reference has already been made to his methods of determining vapour density, and to his mode of ascertaining the melting points of substances fusible only at high temperatures. He also greatly improved the methods of accurately determining the solubilities of substances at various temperatures. His form of water-bath is to be met with in many modern laboratories, surmounted, it may be, with the funnel-shaped cover which he devised to prevent access of dust to the evaporating liquid. Particularly neat and convenient are the drying ovens he constructed in which constant temperatures are obtained by means of liquids of different boiling points, for example, toluene, xylene, anisoil, &c.

Analytical chemistry had little attraction for Meyer, and, beyond his mode of diagnosing primary, secondary, and tertiary alcohols and alcoholic radicles by colour reactions (see p. 180); and the method he devised, with Jannasch, for the simultaneous determination of carbon, hydrogen, and nitrogen in the elementary analysis of organic substances, he made no contribution to this department of the science.

As the director of a large chemical laboratory, and as a laboratory teacher, Meyer worthily followed in the footsteps of Bunsen. In proof of this, I may here quote the testimony of some of our Fellows who have worked under him.

Mr. John I. Watts thus refers to him in the Zürich days:

"Victor Meyer as a teacher had a wonderful faculty of infusing enthusiasm into his students. He was constantly in the laboratory, and whether the pupil was engaged upon the analysis of some simple, well-known substance, or was pursuing original investigation, he seemed somehow to succeed in making him feel how interesting was his work. Possessed of a very quick and active intelligence, he would point out the reason of the difficulties almost before the student had finished recounting them. He was himself a constant worker, and when engaged in his work he always appeared to be in a high state of pleasurable excitement."

Similar testimony is afforded by English chemists who were with him at Heidelberg. Dr. J. T. Hewitt writes:

"Professor Meyer was universally liked by the men who had the privilege of working under him. He had an extraordinary capacity for hard work, and his example, together with the interest he took in his men, induced in them a more or less similar love of work. After the morning lecture, which in the summer semester was at eight, he would come round the laboratory and see how every one was getting on, though of course he spent more time with those who were doing joint work with him than with those who were working with the other professors. We used very often to see him again during the morning, and at least once in the afternoon. In 1891, when I first went to Heidelberg, the most important work being done was on the slow combustion of electrolytic gas, and, not only those who were actually working on this subject, but every one else in the laboratory, used to take great interest in what was going on. Meyer's way of taking up old pieces of his work again and again meant that a very varied sort of work was done in the laboratory; for example, in consequence of Nef's criticism, nitro-fatty compounds were again examined, the result on the students being excellent, in that their general interest in chemistry was aroused. Meyer, as you well know, was an excellent speaker, not only in the lecture room, but in taking the chair at meetings of the Heidelberger Chemische Gesellschaft, when he was seen to great advantage."

Dr. Sudborough, who served him as an assistant when in Heidelberg, writes:

"As organiser and director of the laboratories, Meyer undoubtedly exhibited great business qualities, and everything worked extremely smoothly, owing probably to the fact that his staff had been with him for a number of years and were all on intimate terms of friendship with him. During the time I was an assistant, I had opportunities of observing with what care he entered into even the minutest financial details in connection with the department.

"In the laboratories he was extremely genial and pleasant, always having a kindly word for the students, and taking a great interest in their work. Characteristic, too, was the hopeful way in which he always looked forward to the successful termination of each piece of work, and by this means endeavoured to keep up the interest of the student. Every student who worked under him respected and honoured him as a scientific leader of the first rank, but in addition they felt a deep friendliness towards him on account of the kindly interest he took in them and in their work. A goodly percentage of those carrying out 'Arbeits' under him were either English or American; in fact, Meyer appears to have had a predilection for English and American students.

"Mention must also be made of Meyer's connection with the Heidelberg Chemical Society, of which he was an ardent supporter—in fact, may be said to have been its soul: he and Bernthsen (of the Badische Anilin- u. Soda-Fabrik) were the two presidents in my time and both were frequent contributors."

Dr. Jocelyn F. Thorpe writes:

"Perhaps that which impressed one most about Victor Meyer, besides his power and ability as an exponent and lecturer, was the faculty he possessed of conferring some of his enthusiasm upon the students who worked under him. Be his interest ever so slight and his knowledge of the subject ever so small,

no student could work long with Victor Meyer without feeling that he had a part in a system; that he was, in fact, one of the instruments by which the plans and ideas of a master mind were being shaped. Noticeable, too, was his wonderful power of grasping and remembering every little detail of the researches upon which he was at the moment engaged. At times, as many as thirty men would be working under him on subjects widely varying in character, yet in no case would he forget what each individual had been doing when he last visited him; occasionally he would astonish the student by asking him what had become of some (by the student) long-forgotten substance, the properties of which he could remember most distinctly.

"Every morning after his lecture he would enter the laboratories and personally not only visit the students who were working directly under him, but also those who were engaged in research with the other Professors and Privat-docenten of the department.

"Not only will Victor Meyer live in the memory of those who worked under him as a leader in chemistry, but many will remember him as the genial and kindly host. On many evenings during the semester he would give either supper parties or small dances, and occasionally a ball, to which his students were welcomed, and when his *camaraderie* and great tact were especially noticeable to those of us who, being foreigners newly arrived, were unacquainted with the language and social customs of his country.

"Towards the last his wonderful memory began to fail. I remember meeting him in Heidelberg the year before his death and asking him something, I cannot now remember what, but at any rate he was unable to answer me at the time, and asked me to call and see him the next day. He, however, stopped and tied a knot on his pocket handkerchief, saying, with a sad smile, 'my memory is not what it was.'"

Meyer's literary ability, combined with his power of lucid exposition, made him an admirable writer of what are called popular science articles. He was a frequent contributor to the *Naturwissenschaftlichen Rundschau*, and a number of his essays appeared under the title of "Aus Natur und Wissenschaft" (Heidelberg, 1892). His love of natural scenery and his power of graphically describing it may be seen in his "Märztage in Kanarischen Archipel" (Leipzig, 1893), a record of travel, written during the enforced rest following upon one of his too frequent periods of nervous prostration.

One who had studied him carefully and knew him well thus writes of his personal qualities and of the influence and attraction he exerted upon all who came in contact with him:

"Victor Meyer had a remarkable power over men. Where he entered, there he soon became the centre; each one listened to him, all collected round him. In the fascination he exercised there was nothing intentional or self-conscious; it was far less the influence of a commanding strength than the working of an incomparably attractive and many-sided nature. To this, too, his appearance contributed: the finely chiselled head with the splendid blue eyes might, at first sight, betoken the artist, were it not that there was in the expressive

lectures was blending of the lively temperament with the contemplative calm of the philosopher.

"In the circle of his fellows he captivated all by the eagerness with which he followed anything new, discussing and elucidating it in a manner peculiarly his own; by the joyous, often enthusiastic, recognition of other men's work, and by the warm-hearted interest he displayed in the scientific struggles of his juniors. In society, he showed himself an accomplished conversationalist and *raconteur*, an intelligent and warmly appreciative connoisseur of the arts of music and literature. As a host, he studied the comfort of every guest in his house. At the 'Biertisch' his sunny humour and overflowing wit diffused a general harmony; and his enthusiastic love of natural scenery made him the most delightful of travelling companions." (Paul Jacobson, in *Naturwiss. Rundschau*, **12**, 43 and 44, p. 19).

Meyer's merits were recognised in every land where science is cultivated. He was a corresponding member of the Academies of Munich, Berlin, Upsala, and Göttingen, and an honorary member of many learned societies. The University of Königsberg made him an Honorary Doctor of Medicine. The Royal Society gave him the Davy Medal in 1891.

He was elected an Honorary Foreign Member of our Society in 1883, and attended the celebration of our Jubilee in the spring of 1891. Many of our Fellows will no doubt recall the stirring speech, instinct with a true eloquence, which he made at the banquet in responding to the toast of "Our Foreign Members," with its striking peroration:—"Möge die Chemical Society, neben allen ihren anderen schönen Aufgaben auch in Zukunft ihre völkerverbindenden Ziele in so erfolgreicher Weise anstreben wie bisher, möge Sie blühen und gedeihen als eine Pflegstätte der Wissenschaft, für ihr Vaterland vorerst, aber nicht minder für alle Völker welche sich im friedlichen Wettbewerb wissenschaftlicher Arbeit verbündet wissen."

May this aspiration be fulfilled! May the Chemical Society, in the years to come, continue, as in the past, to recognise, with a full and generous appreciation, the work of those across the seas who engage with us in the friendly rivalry of scientific labour!

And may our action in thus recording the services in our own annals of the gifted man whose

> "prosperous labour fills
> The lips of men with honest praise,"

tend in some degree, however small, to that consummation for which he so earnestly and so eloquently pleaded!

Facsimile

Heidelberg, d. 15 Nov 1865

Meinen besten Dank, lieber
Thurneysen, für Ihren letzten
Brief. Über Ihre Lage kann ich
mich nicht äußern, da ich mich
noch nicht orientiert habe. Das hier
neuere rotierenden Schreib
wirklich bedeutend Fortschritte
macht gefunden hat, habe
mit das ganz unzweifel
haft nach unseren Fortschr
innerhalb und nach Speier
die ist noch ausgestellt ha
im Resultate durch Gross
des Papiers auf der Burgse
zu erhalten. Bei diesen Fort

und meinen letzten Versuchen war aber die Dauer der Expositionen gegen die der Verbrennung nicht selten, wie $\frac{1}{500}$ Sekunde zu 20 Sekunden. Nimmt man nun an, daß die Zerstörung bei dem Chlorsilbergelatine sehr schnell überwunden wird, so können Leichen bei Ihnen Personen nicht mehr sichtbar werden, während sie bei den notwendigen Leichen sehr lange werden mögen. Mit dem neuen Apparat, von dem ich Ihnen sobald

müd sind durch Alles Leuchten
vermittelst lapsen. Leider
ist das Mutter der Not, daß
ihr alle Verwandte zusammen
bis auf diese Zeit haben
aufstehen müssen. In der
Weihnachts- oder Osterfeier
denke ich mit dir einen Appell
alles erneut zu haben, was
wir so lange vergeblich auf
Pfeifel haben. Im Augen-
blicke bin ich mit Knoblauch
mit einer Gemeinschaftlichkeit
Arbeit beschäftigt, die mir
nicht schlafen läßt. Knoblauch
hat nehmlich eine wunder-

Adresse

ganz unerwartete Entdeckung
gemacht, indem er die
Ursache der dunklen
Linien im Sonnenspektrum
aufgefunden und die
Linien künstlich im
Sonnenspektrum verstärkt
hat in linienlosen
Flammenspektren hervor-
gebracht hat und ganz
der Lage nach mit
den Fraunhofer'schen
ideatischen Linien.
Dadurch ist es mir gelungen,
die chemische Zusammen-
setzung der Sonne und

des Tiefpunktes mit derselben
Sicherheit nachzuweisen, wie
wir sie bei der direkten maass-
analytischen Bestimmung, durch
das Ende [illegible] wie bei Titrirmethoden
durch diese Methode mit derselben
Schärfe unterscheiden und dann
messen, wie auf der Tonne
so dass wir z. B. in 20 Grm.
Wasserstoffsuperoxyd noch einen Gehalt
haben nachweisen können, der Existenz
minimaler Tropfen ist durch
Übertragung alles bisher be-
sprochen - vorzuziehen.
Haben wir ein Gemenge von
Na Cl Ba Cl2 so wandern
die Ba Cl Moleküle dem

Tiefpunkte zu, während die Na Cl Moleküle

in meinem Apparate
bewirken, um damit
vermittelst durch ein
Bromsalz alle diese Le-
bensmittel durch
chemische Beobachtung
abzulesen. Einzelne
dieser Reactionen sind
wunderbar scharf. Es
kann man noch $\frac{1}{1000}$
Milligramm Lithium
mit der größten Leichtig-
keit nachweisen. Ich
habe diesen Stoff in fast
allen Pflanzen gefunden.
Freundlich,
Kaupert, Kirchhoff und
alle Freunde lassen beste
Grüße von Ihnen
Ihr
W. Bunsen

BUNSEN MEMORIAL LECTURE.

(Delivered on March 29th, 1900).

By Sir Henry Roscoe, B.A., Ph.D., D.C.L., LL.D., D.Sc., F.R.S., Hon. M.D. (Heidelberg), Corresponding Member of the French Academy of Science, Emeritus Professor of Chemistry in Victoria University, Vice-Chancellor of the University of London.

The death of Bunsen at Heidelberg on August 16th, 1899, severs the last link connecting the chemists of our time with the great men of the earlier part of the century. With Berzelius, of whom Bunsen writes as "my truest friend and counsellor who, during the whole of my scientific life, has stood to me in intimate personal relationship;* with Gay-Lussac, in whose laboratory in Paris he worked in the year 1833; with Dumas, whose acquaintance and friendship he enjoyed when they both were young; with Liebig and Wöhler, who were more nearly his contemporaries, and for whom throughout their lives he entertained the warmest feelings of affectionate regard; with the Berlin chemists Mitscherlich and the two Roses, as well as with the older physicists Dove, Wilhelm Weber, and Magnus, all of whom he counted among his personal friends.

Moreover, living to the ripe age of 88, he was destined to witness the deaths as well as the scientific births of many distinguished colleagues and pupils: of Kirchhoff, Helmholtz, Kopp, and Hofmann; of Strecker, Kolbe, Kekulé, Pebal, Lothar Meyer, and, lastly, of his successor in the Chair of Chemistry at Heidelberg, Victor Meyer. So that, in his later years, Bunsen stood alone in his glory, like some strong oak in the forest which still holds firm root unmoved by the tempests which have smitten down both old and young around it.

Nearly twenty years ago I gave, in the columns of *Nature*, a sketch of the scientific work of him whose memory we are here assembled to honour, as being not merely one of the most distinguished of the great chemists of the century, but one of the truest and noblest of men. In introducing the subject to the readers of that journal, I used the following words, which I make no apology for quoting, as I cannot find more appropriate expressions wherewith to commence the more detailed account of the life and labours of Bunsen in the

* Berzelius, on his side, fully appreciated Bunsen's character and abilities. In 1844 he writes to Schönbein *à propos* of the latter's ozone experiments: "You must devote all your time to this so important investigation, you must follow it up with the true perseverance of a Bunsen, and if possible not abandon it until we are perfectly clear about it." (*Kahlbaum Briefwechsel*, Berzelius-Schönbein, 1898, p. 60).

Memorial Lecture, with the preparation of which the Council of the Chemical Society has honoured me.

"The value of a life devoted to original scientific work is measured by the new paths and new fields which such work opens out. In this respect, the labours of Robert Wilhelm Bunsen stand second to those of no chemist of his time. Outwardly, the existence of such a man, attached, as Bunsen has been from the first, exclusively to his science, seems to glide silently on without causes for excitement or stirring incident. His inward life, however, is on the contrary full of interests and of incidents of even a striking and exciting kind. The discovery of a fact which overthrows or remodels our ideas on a whole branch of science; the experimental proof of a general law hitherto unrecognised; the employment of a new and happy combination of known facts to effect an invention of general applicability and utility; these are the peaceful victories of the man of science which may well be thought to outweigh the high-sounding achievements of the more public professions."

Owing to the fact, not common in the annals of scientific intercourse, that I have enjoyed the privilege for nearly half a century of counting Bunsen amongst my most intimate friends, that we have stood in the position first of pupil and master, and afterwards of colleagues and co-workers, I am in the fortunate position of being able to present to you on this occasion something more than a description of the scientific work which he accomplished, the record of which any one who cares to do so can gather up from his published memoirs. From my personal recollections, I propose to lay before you a picture, doubtless imperfectly, but so far as my abilities go, truly drawn, of the man working in his laboratory, lecturing to his students, and enjoying simple but refined social intercourse with his friends. I shall hope to give you an idea what manner of man he was, what was his moral, as well as his scientific, character, to point out why he was not only venerated as a great leader and teacher, but why he inspired all with whom he came in contact with feelings of deep attachment and regard.

But first let me shortly mention some few particulars of his life, and give you a summary of his most important investigations. Bunsen was born at Göttingen on March 31, 1811. His father, Christian Bunsen,* occupied the position of chief University Librarian and Professor of Modern Philology. After passing through the usual course in the gymnasium at Holzminden in Hanover, Bunsen entered the University in 1828, studied chemistry under Stromeyer (the discoverer of cadmium), obtained his degree in 1830, presenting for this purpose a thesis having the title "Enumeratio et descriptio hygrometrorum." He then visited Paris; arriving there at the latter end of

* Born at Frankfort on April 1, 1770; died March 24 1837.

September 1832, he remained until the spring of 1833, meeting Reiset, Regnault, Pelouze, and Despretz. The latter proposed to Bunsen to work in common at some problem in physical chemistry. Subsequently having visited Berlin and Vienna, continuing his studies and making acquaintance with the scientific men of those cities, Bunsen returned to Göttingen, where, in 1834, he was admitted by the University as Privatdozent in chemistry. In this position he lectured for three semesters, and after Stromeyer's death in 1835, Bunsen temporarily took up his work and lectured six days a week, on theoretical and practical chemistry. In January 1836, he was appointed teacher of chemistry in the Polytechnic School of Cassel as Wöhler's successor. In October 1839, he became Professor Extraordinarius of Chemistry in the University of Marburg, and in 1842 was advanced to the position of Professor Ordinarius. Remaining here until 1851, he went for a short period to Breslau, and in 1852 accepted the chair at Heidelberg, vacated by Gmelin, a post which he occupied until his retirement in 1889. In these several positions, Bunsen laboured incessantly and devotedly for 56 years in the furtherance of chemical science, with the result that his name will be handed down to posterity as one whose work has earned for him the very first rank amongst chemists of the nineteenth century.

On the present occasion, it is not possible to do more than to indicate the nature and extent of Bunsen's work, so numerous are his published investigations, and so wide and far reaching their scope. To bring before you the general effect of the work, and to give you by some examples the special characteristics of that work, is all that can be now attempted. And for these objects I propose to treat the matter rather by classifying his work under separate heads of subjects, than by taking it in the chronological order of publication.

But before commencing a review of some of his most important researches, it may be well briefly to refer to the early work by which he won his scientific spurs. The first paper was one of general interest, as recording his discovery that freshly precipitated hydrated ferric oxide acts as a powerful antidote to arsenical poisoning by rendering the arsenic insoluble both in water and in the secretions of the body. This result of the withdrawal of the whole of the arsenic from solution by this means forms a striking lecture experiment (*Journ. de Pharm.*, 1834, **20**, 567; 1838, **24**, 93).

His next communication shows the interest which, in those early days, Bunsen took in mineralogy and chemical geology, subjects in which he, in after life, became a distinguished exponent. It consisted of an exact analysis and a detailed description of a specimen of allophane from a lignite bed near Bonn (*Pogg. Ann.*, 1834, **31**, 53).

A more specially chemical subject next engaged his attention, namely, an investigation of a new series of double cyanides, in which he not only determined their composition with exactitude but showed the relationships existing between these and other well known members of the same class of bodies. He measured their crystalline form, and proved that ammonium ferrocyanide is isomorphous with the corresponding potassium salt (*Pogg. Ann.*, 1835, **34**, 131; 1835, **36**, 404; 1836, **38**, 208.)

All this work was, however, merely of the nature of what he was in the habit of calling "ein kleiner Vorversuch" when he was indicating the manner in which a pupil should commence an investigation.

The first research in which Bunsen showed his power was the classical one on the cacodyl compounds—begun in Cassel in 1837, and continued in Marburg for no less than six years. The publication of this work placed Bunsen at once in the front rank of experimentalists.

To assist in forming an estimate of the scientific value of these researches (*Pogg. Ann.*, 1837, **40**, 219; 1837, **42**, 145; *Annalen*, 1841, **37**, 1; 1842, **42**, 14; 1843, **46**, 1), it may be well to summon to our aid the opinion of a contemporary whom Bunsen himself, as we have seen, considered as a master, both from a philosophical and from an experimental point of view, the great Swedish chemist, Berzelius.

Those who have studied his celebrated *Jahresbericht* will know that Berzelius was unsparing in his criticism of inaccurate work and of illogical conclusions. The more valuable, therefore, and reliable are his remarks when favourable to the subject under review.

In 1839 (*Jahresber.*, 1839, **18**, 487), Berzelius writes: "An extremely important discovery has been made by Bunsen, in the investigation of the well known fuming, self-inflammable liquid (Cadet's fuming arsenical liquid) obtained when anhydrous acetate of potash is distilled with arsenious acid. From this body, Bunsen has prepared several substances whose properties resemble those of an organic compound, in which, however, arsenic enters as an elementary constituent."

Of the importance of this research as affecting chemical theory, Berzelius reports (*Jahresber.*, 1841, **20**, 526): "In the last German edition of my handbook, I gave what I considered the probable theoretical views regarding this substance, namely, that it contains the compound radicle $C_4H_{12}As_2$, similar to the radicles contained in organic bodies, for which I have suggested to Bunsen the name *kakodyl* in consequence of the nauseous smell of its compounds. With regard to this name, Bunsen writes me as follows: 'The view

of the existence of a ternary radicle $Kd = C_4H_{12}As_2$ agrees so perfectly with the behaviour of the whole alkarsin group that it would be scarcely possible to find a more striking example of a compound radicle. Alkarsin is kakodyl oxide, $\dot{K}d$; it can be directly oxidised and deoxidised. Alkargen is kakodylic acid, $\dot{K}\dot{d}$.'"

In a further notice (*Jahresber.*, 1842, **21**, 503), Berzelius writes: "By this investigation Bunsen has made his name memorable. Chemical science is bound to acknowledge its debt to him for the investigation of a subject at once so important and so dangerous—an investigation of which it may well be said that it leaves little to be desired." Again he reports (*Jahresber.*, 1845, **24**, 640): "Bunsen has now concluded his investigation on kakodyl. Through the private communications with which the author has favoured me, I have been able each year to give an account of the experiments as they progressed. The research is a foundation stone of the theory of compound radicles of which kakodyl is the only one the properties of which in every particular correspond with those of the simple radicles." And he concludes his criticism with a paragraph referring once more to the importance of this tedious and difficult research.

To quote another opinion, that of one of the leaders of modern chemical science, to place side by side with that of the great Swede, I would refer to that expressed by Adolf von Baeyer in his editorial remarks in the reprint of Bunsen's work in Ostwald's collection of scientific classics. "These researches have long been considered classical and they deserve such praise, particularly as pieces of model investigation demonstrating how the most difficult problems of experimental chemistry can be solved by a master's hand."

Amongst the many remarkable new facts which these researches contain is that of the non-poisonous properties of cacodylic acid, although it contains no less than 54 per cent. of soluble arsenic. "A solution of 8 grains of cacodylic acid injected into the *vena jugularis* of a rabbit produced no deleterious result on the health of the animal."

It is also of interest to read Bunsen's description of the properties of cacodyl cyanide, by the explosion of which he lost the sight of his right eye, was nearly poisoned, lying for days between life and death, but the investigation of which he nevertheless brought to a satisfactory conclusion. "It is obtained when cacodyl oxide is distilled with mercury cyanide, when it sublimes to a camphor-like solid; it melts at 32·5° to an oily liquid. The smell of this body produces instantaneous tingling of the hands and feet, and even giddiness and insensibility. The cacodyl compounds appear to exert a specific action on the nervous system. It is remarkable that when one is exposed to the smell of these compounds the tongue becomes covered

with a black coating, even when no further evil effects are noticeable."

Respecting the constitution of the radicle of the cacodyl compounds, various theories have from time to time been put forward. Bunsen himself did not give any opinion on the point, and it was Kolbe who first suggested the view that it was arsine-dimethyl, $As(CH_3)_2$, whilst the experiments of Frankland, and subsequently those of Cahours and Riche, rendered this probable. It is, however, to the researches of Adolf von Baeyer (*Annalen*, 1853, 107, 257), on the arsenmonomethyl compounds that we owe the full explanation of the relation which these various bodies bear to one another.

The cacodyl research claims our interest, not only because, as we have seen, it furnishes us with the first example of an isolable radicle, but also because it assisted Frankland and Kekulé in more exactly illustrating the term "chemical valency." For it is not too much to say that the subsequent researches of Frankland on the organo-metallic bodies, and on the so-called alcohol radicles, as well as those of the French chemists, and, I may add, those of Baeyer, received their first impulse from the cacodyl investigation. This indebtedness was acknowledged by our late lamented Fellow in the graceful and modest words which appear in the dedication of the volume of his collected researches.

"To my friend and teacher, Robert William Bunsen, whose researches on cacodyl, on the gases of the iron furnaces, and on the volcanic phenomena of Iceland, I have always regarded as models of investigation in pure, applied, and physical chemistry, I dedicate these pages both as a testimony of my regard, and in gratitude for the teaching whereby he imbued me with the necessity for thoroughness and accuracy in all scientific work. Would that they were more worthy of such a high standard."

Thus it is seen that although this remarkable research is the only one of any importance which was carried out by Bunsen in the domain of organic chemistry, it was destined to exert such an influence on the later developments of that branch of the science, that he may with truth be regarded as one of the pioneers of modern organic chemistry.

I now pass to an investigation of a different type, but one not less important or interesting than the last.

Up to the year 1838, when Bunsen began his investigation of the composition of the gases of the iron furnaces, the mode of measuring gaseous volumes and the methods adopted for the separation of the several gases was faulty and inaccurate in the extreme. But during the period elapsing between the above year and 1845, Bunsen had not only elaborated and perfected his well-known gasometric methods, but

had applied these methods with signal success to the investigation of the chemical changes which occur in the processes of a most important industry, that of the production of cast-iron in the blast furnace.

The first detailed description of Bunsen's gasometric methods was published in pamphlet form by Kolbe, who was at the time one of Bunsen's assistants. To the English public, these methods became known by a communication made to the meeting of the British Association at Cambridge in 1845 by R. W. Bunsen and Lyon Playfair, entitled "On the Gases evolved from Iron Furnaces with reference to the Smelting of Iron." Before entering upon the technical side of the question, the authors give experimental proofs concerning the accuracy and reliability of the methods employed for the measurement and the separation of the blast furnace gases. One of these consisted in the analyses of a large number of samples of air. These were collected and analysed in Marburg, and gave analytical results upon which Bunsen reports as follows:—"The close agreement of these experiments with one another, and with the result obtained by the careful experimental determination of the composition of air by Dumas, proves that the eudiometric examination of gases admits of a degree of exactness which is certainly not surpassed by the most minute chemical methods, and they further show that the presence of nitrogen does not exert any disturbing influence on the estimation of explosive mixtures of gases."

The report, printed in full in the British Association volume for 1845, next proceeds to discuss the experiments made by Bunsen on the composition of the gases evolved in the process of iron smelting in furnaces fed with charcoal and using cold blast at Vickerhagen, in Germany. From these, it appeared that in such furnaces nearly half the heat of the fuel consumed was evolved in the escaping gases.

The importance of these investigations, as being the first attempt to introduce accurate scientific inquiry into so widespread an industry as that of iron smelting, was at once appreciated by Lyon Playfair, who had made Bunsen's acquaintance at Marburg. In consequence, at Playfair's suggestion, Bunsen consented to visit England, and undertook to carry out a similar set of experiments for the English furnaces fed with coke and coal, and worked both by hot and by cold blast, to those which he had previously made in Germany. Thus was initiated a research which may be truly said to be a model of the application of the methods of scientific investigation to the elucidation of industrial problems. For not only did it clearly reveal the nature of the chemical changes which take place throughout the furnace, but pointed out the direction in which economies, to an undreamt-of extent, might be effected in the processes as then carried on. Thus it proved that whilst about half the fuel was lost as escaping

gas in the German furnaces, no less than 81·5 per cent. was lost in English ones, and, what was important from the industrial point of view, it pointed out that the whole of the heat thus allowed to escape might, without difficulty, be utilised for the various purposes of the works. These suggestions were only slowly adopted by the iron-masters; six years elapsed before any steps in the direction indicated were taken, but gradually the importance of the proposal was appreciated, and now and for many years past the whole of the hitherto wasted heat has been utilised, and economies effected of which the value may be reckoned by millions rather than by thousands of pounds.

Not only is it the lost heat which has been recovered, but also valuable bye-products, the existence of which had been, up to that time, entirely ignored. The report points out the loss of combined nitrogen —both as ammonia and cyanogen—which the process as then carried out evolves, the upper part of the furnace being, in the words of the report, "a region of distillation and not of combustion." The amount of loss of these valuable materials was ascertained by accurate analysis, and a method for recovering them suggested, "without increasing the cost of manufacture or in the slightest degree affecting the process of smelting." *A propos* of the determination of the escaping cyanogen compounds, the occurrence of a singular accident to Bunsen, as related by Playfair, is found in the admirable life lately written by Wemyss Reid. "Bunsen was engaged below," at the blast furnaces at Alfreton, in Derbyshire, "and I above, passing the gases through water to collect any soluble products, when I was alarmed by being told that my friend had become suddenly ill. I ran down and saw white fumes coming out of a lateral tube, and Bunsen apparently recovering from a fainting condition. I applied my nose to the orifice and smelt the vapour of cyanide of potassium, which gave an entirely new light to the processes of the furnace."

In 1857, Bunsen collected in a volume—the only book he ever published—the whole of his gasometric researches, and of this a second and greatly enlarged edition appeared in 1877 ("Gasometric Methods," by R. W. Bunsen, translated by H. E. Roscoe, 1857). No better or more complete method of learning what Bunsen's work is like can be taken than that of reading this volume. For originality of conception, for success in overcoming difficulties, for ingenuity in the construction of apparatus, and for accurate work, I believe the book, as a record of experiment, to be unequalled.

The first part contains a description of his various processes for collecting, preserving, and measuring gases, different methods being employed for the first of these according to the source from which the

gases are obtained, whether, as has been described, from blast furnaces, or from fumeroles, from volcanic vents, or when freely rising from mineral springs, or whether the gases are contained in solution in river- or spring-water. In the second part, we find a full description of the methods of eudiometric analysis, giving details of manipulation, with a discussion in each case of the probable sources of error and of the means of their limitation. As a model of accurate work (his oxygen determinations in air showed differences of 0·1 per cent. on the oxygen), Bunsen's eudiometric methods will always remain as the standard. More expeditious and simpler methods have been introduced of late years, but none of these equals the original processes in exactitude.

The third portion of the volume consists of a description of two new methods for determining the specific gravity of gases. The first of these, which also applies to the case of vapours, consists in weighing a tared vessel, filled first with the gas or vapour under examination and then with air, all variations due to change of temperature and pressure being eliminated by a simple and ingenious compensating arrangement. Perhaps the most interesting portion of this section is a description of a new thermostat, by means of which perfectly constant temperatures up to a high point can be obtained. This served Bunsen for ascertaining the specific gravity of aqueous vapour at different temperatures, and closely accordant numbers were obtained, although the weight of vapour amounted to only 80 mgm. The second method, applicable only to gases, depends on the determination of the rates of diffusion of the gases into air. Here, too, the volume of gas operated upon need not exceed 50—60 c.c., and yet the results obtained are extremely accurate. On this point, Bunsen remarks that for technical purposes, as, for example, for the determination of the density of coal-gas, the above simple method will probably be found preferable to all other processes.

The fourth part contains a series of investigations on the absorptiometric phenomena of gases in water and alcohol, the experiments having been chiefly undertaken with a view of determining the limits to which the well-known laws of pressure hold good. First he describes his absorptiometer, a new instrument by means of which it is possible to obtain accurate numbers with relatively small volumes of the gases. The absorption-coefficients of no fewer than 27 different gases in water and alcohol were determined by methods varying according to the nature of the case, partly carried out by himself and partly by many of his pupils, the result being that certain gases, generally those least soluble in water, are found to be in accord with Dalton's law of pressures and Dalton and Henry's law of partial pressures, whereas the more soluble gases are not always in accord with them. In the former

class, it is possible, from an experimental determination of the coefficient of absorption, to calculate the composition of the original gas, the composition derived from an absorptiometric analysis being found to agree exactly with that obtained by direct eudiometric measurements. It is also possible to ascertain whether a given gas consists of a single substance or is a mixture of several. Thus whilst eudiometric analysis cannot decide whether the gas evolved by the action of caustic alkali on an acetate is methane or a mixture of equal volumes of ethane and hydrogen, this can readily be accomplished by absorptiometric methods.

In the fifth part of the volume he discusses the phenomena of gaseous diffusion, and, although admitting the truth of Graham's law for cases of pure diffusion, he obtained results, when a stucco diaphragm of considerable thickness is used, which are not in accord with this law, the conclusion being that the pores of gypsum act upon gases, not as a series of fine openings, but rather as a series of capillary tubes, the phenomena being thus modified by those of transpiration. At the end of this chapter, he describes the details of a method for ascertaining, by diffusion, whether a given gas is a mixture or not.

The sixth and last section relates to the combustion phenomena of gases. The temperature of combustion, that is, the temperature of the interior of a mixture of burning gases, can be calculated from the heat of combustion of the gaseous mixture and the specific heats of the products of combustion under the assumption that the combustion at this high temperature is perfect. This condition, however, is not fulfilled, and Bunsen therefore endeavoured to determine this temperature by another means, namely, by measuring the pressure produced at the moment of explosion of an enclosed gaseous mixture.

For this purpose, he constructed a wonderfully simple apparatus, by means of which he ascertained that the maximum temperature of combustion of carbon monoxide and of hydrogen with the theoretical volume of oxygen was respectively 3033° and 2844°. He likewise attempted to determine the rate at which the explosion is propagated and came to the conclusion that for hydrogen and oxygen this was 34 metres per second. Subsequent experiments, especially those of Dixon (*Phil. Trans.*, 1893, **184**, 97) have shown that this rate referred only to the initial period of the combination before the explosion wave had attained its maximum velocity, this latter amounting in the case of hydrogen and oxygen to the high number of nearly 3000 metres per second, the rate in other gases being of the same order in magnitude, and the ignition appearing to be propagated in somewhat the same manner as a sound wave.

One of the best known of Bunsen's discoveries is that of the carbon-zinc battery, which bears his name.

The construction of this battery in 1841 (*Annalen*, 1841, **38**, 311) marks an era in the economic production of electricity. By the replacement of carbon for the platinum plates of Grove, Bunsen not only greatly reduced the initial cost, but increased the length of time during which the current can be maintained at its maximum. The success of the invention depends upon a method he devised for overcoming the disintegrating action on the carbon of concentrated nitric acid. This he effected by strongly igniting the cylinders, thus foreshadowing the process adopted on a large scale for graphitising the carbon poles now so generally used for electro-industrial purposes by ignition in the electric furnace. It is interesting to remember that it was Bunsen who, so early as 1843, pointed out that the electric current could be made use of as a means of illumination. He describes how, by using a battery of 44 of his elements, a light equal in illuminating power to 1171·3 candles can be obtained for an expenditure of 1 lb. of zinc per hour, and giving a light "the brilliancy of which the eye can scarcely support." He adds that by enclosing the carbon poles in a globe of glass, the wear of carbons by oxidation might be minimised. In short, he describes the first step towards the modern system of arc lighting rendered generally applicable on the large scale by the discovery of the dynamo. In his first communication respecting this battery, Bunsen gave a careful estimate of the work which it can accomplish. He showed that three cells will, in 30 minutes, decompose 0·6775 gram of water yielding 1137 c.c. of mixed gas measured at 0° and 760 mm. The corresponding loss of zinc in each cell was then determined, the result showing that the same weight was dissolved in each, and that the weights thus found correspond closely with the zinc equivalent for the above amount of water decomposed. A few years later, in 1848, he determined the electro-chemical equivalents for zinc and water. For the first of these, he obtained the value 0·033, and for the latter 0·00927; in other words, in order to decompose 1 mgm. of water per second, a current of the absolute intensity of 106·33 is necessary. These experiments confirm Faraday's law, showing that the quantity of water decomposed is proportional to the quantity of circulating electricity, and that the nature of the poles, as well as the conducting power of the liquids decomposed, exert no influence on the result.

We owe to Wilhelm Weber the first determination of the scientific units for electrical measurements, and in 1840 he obtained the number 0·009376 for the electrochemical equivalent of water with his unit-current. The difficulties which surround the subject are:

(1) the measurement of the current, and (2) the absorption of the decomposed gases by water and electrodes, and (3) the production of ozone. Bunsen improved the voltameter by evolving the mixed gases from hot acidified water by which the second and third of these difficulties were overcome. At present, voltameters depositing copper or silver are employed, and the ampère, which is now our practical unit, is one-tenth of that used by Weber and Bunsen, so that the electrochemical equivalent of water is 0·0009315 gram, meaning that one ampère decomposes that amount of water in one second.

This, however, was only the beginning of the work which the Bunsen battery was destined to perform. It was not until 1852, when in Breslau, that Bunsen turned his attention to using the battery for the electrolytic preparation of metals, some of which had not then been obtained in a coherent condition, and others had only been prepared in such minute quantities that their physical and chemical properties could not be properly studied. The first of these metals he attacked was magnesium (*Annalen*, 1852, **82**, 137), the reduction of which had vainly been attempted by Davy, and only with very partial success by Bussy in 1830. The difficulty which had hitherto stood in the way, was the fact that the globules of molten magnesium are lighter than the fused magnesium chloride used as the electrolyte, and that on their formation they rise to the surface and burn. To avoid this, Bunsen adopted the ingenious plan of cutting the carbon pole, on which the metal forms, into pockets, inside which the magnesium is deposited, and from which the molten globule cannot escape. By means of the tangent galvanometer, Bunsen measured in absolute units the electricity employed, finding that the quantity of magnesium reduced is 2·45 grams, whilst the theoretical yield of metal is 4·096 grams. Having obtained the metal in some quantity, he determined its physical and chemical properties, showed how it could be pressed out into wire, and measured the luminous intensity of the burning metal. This he found to be 500 times that of a candle flame.

Some seven years later, he and I measured the actinic value of the light emitted by burning magnesium, and showed that it could be used for photographic purposes. We found that a burning surface of magnesium wire, which, seen from a point of the sea's level, has an apparent magnitude equal to that of the sun, effects, at that point, the same chemical action as the sun would do if shining from a cloudless sky at the height of 9°53′ above the horizon. On comparing the visible brightness of these two sources of light, it was found that the brightness of the sun's disc, as measured by the eye, is 524·7 times as great as that of burning magnesium when the sun's zenith-distance is 67°22′, whilst at the same zenith-distance the sun's *chemical brightness* is only 36·6 times as great. Hence the value of this light as a

source of chemically active rays for photographic purposes is at once apparent. The application of magnesium as a source of light has become of technical importance. A burning magnesium wire of the thickness of 0·297 mm. evolves as much light as 74 stearin candles, of which five go to the pound. If this light lasted one minute, 0·987 m. of wire weighing 0·120 gram would be burnt. In order to produce a light equal to 74 candles burning for 10 hours, whereby 20 lbs. of stearin is consumed, 72·2 grams or $2\frac{1}{2}$ oz. of magnesium would be needed. The light from burning magnesium has been employed for signalling, and for military and naval purposes, and it is especially used in pyrotechny.

Perhaps the most interesting of these applications of the battery is that of the preparation of the metals of the alkaline earths (*Journ. de Pharm.*, 1854, **26**, 311; 1855, **28**, 155), the isolation of which had hitherto eluded pursuit, and this work he handed over to our countryman, Augustus Matthiessen, who, under Bunsen's guidance, brought the investigation to a successful issue. The conditions most favourable to a reduction were carefully worked out. It had already been pointed out by Bunsen "that the density of the current (that is, the current per unit cross section) is the chief condition under which the electricity is able to overcome chemical affinities." This condition was fulfilled by using for the negative pole a very short length of thin harpsichord wire, upon which the reduced metal hangs in the form of molten beads, from which they can be quickly detached and plunged into petroleum. Another necessary condition is that the melting point of the electrolyte should be as low as possible, and this was attained by using a mixture of the chlorides of calcium and strontium, and by the addition of some sal-ammoniac to the mass as the electrolysis proceeds. This subject was again further elaborated, in 1875, in the Heidelberg laboratory by Hillebrand and Norton (*Pogg. Ann.*, 1875, **156**, 466), who prepared considerable quantities of cerium, lanthanum, and didymium in the coherent metallic state.

But the reduction of the metals was not the only important work which Bunsen got out of his battery, for quite early in its history it made its mark in organic chemistry. If by the electrolysis of caustic soda we obtain oxygen and a metallic radicle, might not the electrolysis of an organic substance yield the corresponding organic radicle? Doubtless a question of this kind presented itself to Bunsen's mind when he set his assistant, Kolbe, to work on the electrolysis of acetic and valeric acids (*Annalen*, 1847, **64**, 339; 1849, **69**, 257). The results of investigations thus commenced and carried out, both by Kolbe alone, and in collaboration with Frankland, and the still more prolific researches of the latter chemist, are matters of scientific history; it

is, however, not so generally recognised that they owe their origin to the Bunsen batter

In addition to the zinc–carbon–nitric acid battery, Bunsen also constructed a powerful thermopile of copper pyrites and copper (*Pogg. Ann.*, 1864, **123**, 505); and in later years a constant zinc–carbon–chromic acid battery (*Pogg. Ann.*, 1875, **155**, 232) so arranged that the zinc and carbon plates could be lowered readily into the exciting liquid, and thus the battery was easily put in and out of action. This he used for obtaining the spark spectra of the rare earth metals.

For the purpose of measuring the intensity of the light given off by carbon-poles connected with his battery, Bunsen, in 1844, constructed his well-known photometer (*Berzelius Jahresber.*, 1845, **24**, 13). The essential feature of this apparatus is the 'disc' of paper having a greased spot in the centre, or having a greased circumference with an untouched spot in the middle. With regard to this, Elster relates the story that when he showed this arrangement to the late Emperor Frederick, then Crown Prince, the Prince remarked, "For the first time in my life, I now know the value of a spot of grease." In the original Bunsen photometer, a small flame burning in a closed box fixed on a pivot in the centre of a long board, illuminated the back of the disc, the relative luminous intensity of the two sources of light under examination being ascertained by moving them alternately backwards and forwards on each side of the disc until, in each case, the spot disappeared. This form of the photometer was afterwards modified by other observers, not, according to Bunsen, to its advantage, by omitting the small flame and box, and simply moving the disc backwards and forwards between the two fixed sources of light. Recently, Preece has proposed to reintroduce the principle of the original Bunsen arrangement of ascertaining the relative luminosity by always exposing the same side of the disc, and therefore eliminating the error arising from its translucency. In one form or other, the Bunsen photometer has, however, for many years been in general use, but recently it has been partially replaced by the shadow photometer.

In this connection, mention must be made of two important researches of a physical rather than of a purely chemical nature, and characteristic of the manipulative as well as of the intellectual power of the author. They refer to the ice- and the vapour-calorimeters.

As, by means of his battery, it was possible for Bunsen to prepare small quantities of the rare metals, so by help of his ice calorimeter (*Pogg. Ann.*, 1870, **141**, 1) he was able to ascertain one of their most important physical properties. It was constructed in order to be able

to determine exactly the specific heats of substances which could only be obtained in small quantities, and to which the usual calorimetric methods were therefore inapplicable. Thus it became of the greatest theoretical importance to ascertain the specific heat of indium, of cerium, lanthanum, didymium, and germanium, and other metals which are only obtainable in small quantities. The principles of construction and mode of action of the ice calorimeter are so well known that a description of the instrument and its use is here superfluous. They were published in 1870, and by its means the atomic weight of indium and the formulæ of its compounds were rectified, whilst the doubts arising as to the formulæ of the compounds of other metals were eliminated. "Thus Bunsen largely contributed to the confirmation, and to the acceptance of the system of atomic weights now in use, and thereby to the rational classification of the elements depending on that system." *

In 1887, when 76 years of age, Bunsen published the description of a new vapour calorimeter (*Ann. Phys. Chem.*, 1887, **31**, 1), upon which he had for some time been engaged. It depends on the same principle as the one previously constructed by Joly (*Proc. Roy. Soc.*, 1886, **41**, 352). The body whose specific heat has to be determined is hung by a fine platinum wire to the beam of a balance, then brought into saturated aqueous vapour at 100° and the amount of water deposited on the body whilst it is being heated is weighed in the vapour, this amount being directly proportional to the specific heat. This method gives very accurate results, and differs in some essential respects from that proposed by Joly. In this way, Bunsen determined the specific heat of platinum at different temperatures, that of glass, and of water enclosed in glass. This latter he found to be 0·9992 (Joly obtained as a mean result 1·0062). The originality of this idea, arrived at quite independently from Joly, and the degree of accuracy with which the whole research is worked out, must indeed be considered as a wonderful achievement of a man close upon 80 years of age.

In addition to the work which Bunsen did alone, I am bound to refer to the long and difficult series of researches on the measurement of the chemical action of light, in all of which I was associated with him. (*Pogg.*, 1855, **96**, 373; *Phil. Trans.*, 1857, **147**, 355, 381, 601; 1859, **149**, 879; 1863, **153**, 139). For this reason, I feel difficulty in criticising it. This difficulty is, however, somewhat removed if, for this Lecture, I simply quote the opinion of Richard Meyer as found in his 'Nachruf' of Bunsen, with an extract from Ostwald's "*Classiker*" with which he closes the notice, and as an illustration of Bunsen's literary

* Stanislao Cannizzaro, Commemorazione del Socio Straniero. R. W. Bunsen, *Rendiconti d. R. Acad. dei Lincei*, 8 December, 1899. Roma, 1899.

style, add a few sentences of the introduction which he wrote to the fourth part of our photochemical researches.

"The year 1855 was rendered especially memorable, as in that year the first communication appeared of the photochemical investigations which Bunsen carried out together with H. E. Roscoe. These researches are considered by Ostwald simply as 'the classical example for all further researches in physical chemistry.'

"The investigation is founded on the discovery by Gay-Lussac and Thénard of the action of light on a mixture of equal volumes of chlorine and hydrogen, in which an intense illumination produces an explosive combination, whilst with a less intense one the combination proceeds more slowly. So early as 1843, Draper had made use of this property for the construction of an actinometer, to which he gave the name of tithonometer. This, however, first became a reliable instrument in the hands of Bunsen and Roscoe. Equipped with this instrument, they have determined the most important laws of the chemical action of light after overcoming extraordinary experimental difficulties. Subsequently they replaced this apparatus, in consequence of the difficulties attending its manipulation, by the much more convenient chloride of silver actinometer.

"The first point determined was that the chemically active rays are reflected and absorbed according to the same laws as the visible rays, and that their intensity diminishes as the square of the distance. The question as to 'whether energy is expended in the act of photochemical combination for which an equivalent amount of light disappears, or whether the action, like that of the liberation of a spring, is brought about by the chemical rays without any appreciable loss of light,' is decided in favour of the first view; the phenomenon is termed by the authors photochemical extinction.

"A second, very remarkable phenomenon, first pointed out by the authors, is that of chemical induction. This refers to the fact that the action of light on the sensitive mixture of chlorine and hydrogen does not begin in its full intensity, but that it slowly increases, until after the lapse of a certain time it attains its regular and maximum rate. A satisfactory explanation, much less a theory, of induction is as yet wanting. Lastly, it was proved that photochemical action depends solely upon the quantity of the incident light, and is altogether independent of the time during which the insolation takes place.

"The great and important influence which photochemical action exerts in organic nature, especially in plant assimilation, renders the application of photochemical measurements to meteorological and climatic phenomena of special interest. But the difficulties which surrounded such an application were enormous. In the first place, it was necessary to find a unit of absolute measurement for the chemi-

cally active rays. A flame of carbonic oxide which emits chemically active rays of great intensity, burning in air under carefully specified conditions, satisfied the requirement. It was found that whilst the variation of the chemical action of the light reflected from a clouded sky was subject to no recognisable law, that obtaining when the sky was cloudless, and when direct sunlight was employed, at once exhibited distinct relations. The curves of daily intensity thus obtained before and after noon were seen to be symmetrical throughout the day; in direct sunshine, these curves of course rise much higher than is the case in diffuse daylight, moreover, the considerable variation due to change of latitude was precisely calculated.

"The dependance of the chemical action on the wave-length of the incident light was carefully studied, the result being that the most intense action was exerted by the rays between the lines G and H of Fraunhofer; the curve falls sharply towards the red end of the spectrum, whilst it extends in the more refrangible portion far into the ultra-violet. Strictly speaking, this only applies to the mixture of chlorine and hydrogen, still experiment has shown that the same thing is to some degree true of many other sensitive substances, although the distribution of the chemical activity in the spectrum is a different one.

"This short account of the photochemical researches is far from doing them justice. 'In no other research in this domain of science do we find exhibited such an amount of chemical, physical, and mathematical dexterity, of ability in devising experiments, of patience and perseverance in carrying them out, of attention given to the minutest detail, or of breadth of view as applied to the grander meteorological and cosmical phenomena of nature' (Ostwald)."

[And now comes Bunsen's introduction:—

"The measureless store of energy which nature has amassed in the sun's body flows in an unceasing current as solar rays throughout the universe.

"The labour expended on the earth's surface in the maintenance of the animal and vegetable creation, and in the production of geological change, is derived, almost exclusively, from this source.

"Those of the sun's rays which vibrate most slowly, and form the red portion of the solar spectrum, including the rays visible and invisible which surround them, give rise by their absorption, more especially to the thermic actions observed on the surface of the earth, and in both the fluid zones which as ocean and atmosphere encircle the solid crust of our planet. These rays constitute the sources of heat which, in those grand processes of distillation and atmospheric deposit, have effected these vast transformations of the earth's crust, by the study of which we obtain some idea of the immensity

of the sun's action exerted during geological ages upon our globe.

"Of a totally different kind, on a scale less magnificent, but not less important, are the effects mainly produced by the more highly refrangible, and more rapidly vibrating, portions of the solar rays. These rays exert the most marked influence upon the chemical changes on which the vegetable world depends, and are therefore of the greatest importance as regards the character and geographical distribution of organic nature.

"Although the atmospheric phenomena regulating the amount and distribution of the chemical action of light on the earth's surface have not as yet been systematised to the same extent as the thermic, electrical, and magnetic phenomena of meteorology, the reason is not so much that their importance has been overlooked, as that the difficulties which surround an exact investigation of the subject have up to the present time proved insurmountable. . . . The light which the sun radiates into space during each minute of time represents a chemical energy, by means of which more than twenty-five and a half billions of cubic miles of chlorine and hydrogen may be combined to form hydrochloric acid" (*Phil. Trans.*, 1859, **149**, 879).

Of all Bunsen's researches, the one which will undoubtedly stand out pre-eminent as time rolls on is that on Spectrum Analysis.

The most important discovery made by Bunsen during the short duration of his residence in Breslau was the discovery of Kirchhoff, who was then Professor of Physics in that University, and whose great ability the elder man at once recognised. No sooner had Jolly removed to Munich in 1854 than Bunsen took care that Kirchhoff should be his successor in the Heidelberg Chair of Physics. And thus came about that great twin research which has made the name of these men known through the wide world. To dilate upon the importance of the discovery is unnecessary; to follow out the growth of this branch of science in its height and depth and breadth is here impossible. All that can be now done is to indicate briefly the origin of the discovery and to refer to a few points in Bunsen's work which are of special interest to chemists. To begin with, let me give you in Bunsen's own words the account of Kirchhoff's great discovery—namely, the full explanation of Fraunhofer's lines in the solar spectrum, pointing the way to a knowledge of the chemical composition of the sun and fixed stars, and then of his own application of the principles of spectrum analysis to the examination of terrestrial matter.

In a letter to myself,* dated November 15, 1859, he writes:

* A facsimile reproduction of the whole of this letter is inserted at page 536.

"At the moment I am engaged in a research with Kirchhoff which gives us sleepless nights. Kirchhoff has made a most beautiful and most unexpected discovery: he has found out the cause of the dark lines in the solar spectrum, and has been able both to strengthen these lines artificially in the solar spectrum and to cause their appearance in a continuous spectrum of a flame, their positions being identical with those of the Fraunhofer's lines. Thus the way is pointed out by which the material composition of the sun and fixed stars can be ascertained with the same degree of certainty as we can ascertain by means of our reagents the presence of SO_3 and Cl. By this method, too, the composition of terrestrial matter can be ascertained, and the component parts distinguished, with as great ease and delicacy as is the case with the matter contained in the sun; thus I have been able to detect lithium in 20 grams of sea-water. For the detection of many substances, this method is to be preferred to any of our previously known processes. Thus, if you have a mixture of Li, Ka, Na, Ba, Sr, Ca, all you need to do is to bring a milligram of the mixture in our apparatus in order to be able to ascertain the presence of all the above substances by mere observation. Some of these reactions are wonderfully delicate. Thus it is possible to detect $\frac{5}{1000}$ of a milligram of lithium with the greatest ease and certainty, and I have discovered the presence of this metal in almost every sample of potashes."

The following letter contains the first announcement of his discovery of cæsium. It was not until one month later (May 10, 1860) that the fact of the discovery was communicated to the Berlin Academy of Sciences:

Heidelberg, April 10, 1860.

"My dear Friend,

"Weltzien went to Paris a week ago and pressed me to accompany him, but unfortunately I was unable to free myself from work which I had postponed until the vacation, and so I have been obliged to forego the pleasure of seeing you in Paris and to tell you how much I have been pleased with your investigation. Do not be annoyed with me, dear Roscoe, that I have done nothing with our light investigation. I have left everything untouched, because I have obtained full certainty, by means of spectrum analysis, that besides Ka, Na, and Li, a fourth alkali metal must exist, and all my time has been occupied in endeavouring to isolate some compounds of the new substance. Where the presence of this body is indicated, it occurs in such minute quantity that I almost give up hope of isolating it unless, indeed, I am fortunate enough to find a material which contains it in larger amount."

On November 6, 1860, Bunsen describes to me his further work on the new metal as follows:

"I have been very fortunate with my new metal. I have got 50 grams of the nearly chemically pure chloro-platinic compound. It is true that this 50 grams has been obtained from no less than 40 tons of the mineral water, from which 2·5 lbs. of lithium carbonate have been prepared by a simple process as a bye-product. I am calling the new metal "cæsium," from "cæsius" blue, on account of the splendid blue line in its spectrum. Next Sunday I hope to find time to make the first determination of the atomic weight."

The rare combination of mental and manual dexterity characteristic of Bunsen is nowhere more strikingly shown than in the investigation of the cæsium compounds. From these 17 grams of cæsium chloride obtained as above described, he not only succeeded in preparing and analysing all the more important compounds, but in crystallising the salts in such a form that he was able to determine their crystallographic constants and then to supply all the necessary data for fixing the position of this new element and its compounds in relation to its well known relatives potassium and sodium.

All the world knows that shortly after his discovery of cæsium the birth of another new alkali-metal, rubidium * (*Berlin Monatsh.*, 1861, 6, 273), was announced by Bunsen, and the application of spectrum analysis led, in other hands, to the isolation of thallium in 1861, indium in 1863, germanium in 1886, gallium in 1875, and scandium in 1879, but alongside of these came announcements of the discovery of other new metals whose existence was more than doubtful. Concerning these he writes to myself: "The frivolous way in which new metals are now discovered by dozens and sent forth into the world duly christened is certainly no gain to science; only later inquirers will be able to decide what remains new and serviceable out of this chaos of material."

I may here remind you that cæsium is not only interesting as being the first metal to have been discovered by spectrum analysis, but because, even before Bunsen's discovery, chemists had worked with cæsium salts which they had mistaken for potassium compounds, so closely do the properties of the two metals correspond. Plattner, in 1846, analysing a mineral from Elba termed pollux, could not bring his analysis to add up to 100 parts and was unable to explain the anomaly. After Bunsen had established the existence of cæsium, Pisani, in 1864, took up the re-examination of the mineral, and showed that the alkali-metal was cæsium, with an atomic weight of 131·9, and not potassium with one of 38·85, and thus accounting for the missing percentage.

* Aulus gellius noctes Atticæ II. 26. "Rubidius autem est rufus atrior et nigrore multo inustus."

In the Christmas vacation of 1863, an extraordinary accident, illustrating in a painful manner the close analogy which exists between the properties of the potassium compounds and those of rubidium, occurred in Bunsen's laboratory. It is thus described in a letter from Bunsen to myself:

"For a week I have been in a very depressed and sad state of mind owing to a fearful misfortune which has taken place in the laboratory. During my absence from Heidelberg in the Christmas holidays, a man employed there in cutting wood, in spite of previous warnings, inexcusably took his little son with him into the laboratory and allowed him to run about without proper supervision. The child seems to have put into his mouth an iron tube which had been used for the reduction of metallic rubidium by heating the carbonate with charcoal, and in which the explosive compound carbonic-oxide-rubidium had been formed. The result was that an explosion occurred, and although no mechanical wounding took place, the child's throat and roof of its mouth were fearfully burned, so much so that it died within twelve hours. You can imagine how much I have been affected by this accident, although, Heaven be thanked, no blame for want of caution can be attributed to me."

In 1875 (*Pogg. Ann.*, 1875, **155**, 230, 366), Bunsen published a long investigation upon the spark spectra of the rare earths. He had constructed, and describes there, a new and convenient form of carbon-zinc chromic acid battery which was sufficiently powerful to give a small arc light or to work a large induction coil, and could be put in and out of action, so that it was made ready for instant use by lowering the carbons into the exciting liquid. By the help of this battery, Bunsen mapped the spark-spectra of the rare earths, the separation of which has proved to be a tedious and very laborious piece of work. An accident, almost pathetic in its incidents and somewhat similar to the well-known accident which happened to Newton's manuscript, occurred to Bunsen. He had just completed the above-named research and the finished manuscript lay upon his writing table. On his return from dinner one day, he found the whole reduced to ashes! It seems that a spherical water-bottle stood on his desk, and this, acting as a lens in the sunlight, was the cause of the disaster. Writing to me on June 3, 1874, he says:

"You have good cause to be very angry with me for not having answered your sympathetic letter before this; but I have not allowed myself lately to think of anything which would remind me of the loss of my burnt research. . . . I had finished the editing of a memoir on a subject which had occupied me for three years, and was about to forward it to Poggendorff for publication, when on returning home the other day I found all these papers, which had caught fire during

my absence, reduced to ashes. The photographs of the apparatus, the drawings of the spark-spectra of the metals of the rare earths, to separate and map which had cost me untold trouble, all are burnt." With regard to this accident, Kirchhoff writes to me on May 22: "The disaster of which you read in the papers really happened. The manuscript of a research at which he had laboured for years, with maps of spectra, has been burnt. He was, to begin with, much depressed, but his wonderful elasticity of mind enabled him to overcome his dejection, and he has already begun to replace what was lost." This he continued to do, never drawing rein until the memoir was again ready for press.

The original views of Bunsen and Kirchhoff concerning the nature of the spectra of the alkali and alkaline-earth metals as examined in the flame of the Bunsen burner has since their time undergone considerable modification. We now know that whilst the spectrum of potassium, sodium, cæsium, rubidium, and lithium, produced when any compound of these elements is brought into the flame, is that of the metal, it is quite otherwise with the similar spectra of the alkaline earths, for if a bead of calcium, strontium, or barium salt be brought into the flame, bright lines and bands are seen characteristic indeed of the individual substance, but differing altogether from the spectra obtained from the above compounds at the high temperature of the electric spark. In the first case, we are dealing with the spectra of a compound, whereas in the latter instance we obtain the line spectrum of the metal itself. Nor must it be forgotten that Bunsen was the first to point out that which has only in recent years been fully recognised, namely, that change of physical condition under which a spectrum is observed may give rise to fundamental changes in the character of the spectrum itself. It was in his research on the absorption spectrum of didymium (*Pogg. Ann.*, 1866, **128**, 100), carried out with minute care, that this point was made clear. In this he proved that, examined under a high dispersive and magnifying power, a crystal of didymium sulphate gives an absorption spectrum in which the dark bands vary in position and in breadth according to the position of the crystal in regard to its axes through which the light passes, that is, whether the polarised ray is ordinary or extraordinary. These changes, somewhat similar to those since shown to be effected by change of pressure under magnetic influence, or from change of temperature, have yet to receive a satisfactory explanation. To enlarge upon these matters is, however, beyond the province of the present address, suffice it to say that Bunsen's original investigation has opened out an unbounded field for research the cultivation of which has already yielded great results and will in future yield still greater ones.

Next let us turn to his celebrated researches on chemical geology, especially those concerning the volcanic phenomena of Iceland.

The only relaxation from his scientific labours which Bunsen throughout life allowed himself was travelling, and this he thoroughly enjoyed. During many autumn vacations, I had the pleasure of accompanying him in rambles throughout Switzerland and the Tyrol. He walked well and had a keen appreciation of natural beauty, especially of mountain and woodland scenery, whilst he took great interest in the geology and physical characteristics of the districts through which he passed, and this it was that led him to turn his mind to chemico-geological studies. So early as 1844, in company with Pilla and Matteucci, he visited and carefully examined the carboniferous deposits occurring in the well known fumerole districts of the Tuscan Maremma (*Annalen*, 1844, **49**, 264), and in 1846 he undertook his journey to Iceland, where he spent 3½ months, and the outcome of which was the well-known series of investigations on the volcanic phenomena of that island (*Annalen*, 1847, **62**, 1; 1848, **65**, 70). No doubt it was the eruption of Hecla in 1845 which served as the incentive to this expedition, for he desired, not only to examine the composition of the Icelandic rocks, which are entirely of volcanic origin, but especially the pseudovolcanic phenomena which present themselves in greater force immediately after a period of activity than at other times.

The expedition to Iceland was an official one promoted by the Danish Government. Bunsen was accompanied by Sartorius von Waltershausen and Bergman, both colleagues at Marburg, as well as by the French mineralogist Des Cloizeaux. They left Copenhagen on May 4, 1846, reaching Reykiavik after a short but stormy passage of 11 days. The party spent 10 days at the foot of Hecla, where Bunsen collected the gases emitted by the fumeroles, and investigated the changes which these gases effect on the volcanic rocks with which they come into contact. Eleven more days were given to the investigation of the phenomena of the geysers, and at the end of August Bunsen left the island, having in the short space of about three months collected a mass of material the working up of which, as he writes to Berzelius, "will tax all my energies for some length of time," a prediction which was subsequently fully realised.

Connected with the Icelandic expedition, the following story is told:—Bunsen had made all his arrangements for the expedition, had packed all the apparatus required for carrying on an experimental research in those regions, but he had been unable to obtain from the Kurfürst of Hesse-Cassel, of whose Civil Service he was a member, leave of absence from his professorship, although the application had been made repeatedly. In this difficulty, he appealed for help to a

cousin who happened to be domestic physician to this Prince, whose eccentricity was well known. The difficulty was solved as follows: the physician informed his Royal Highness that a cousin of his who was professor of chemistry in the Marburg University had conceived the wild idea of voyaging to Iceland, and that this was regrettable inasmuch as the professor would inevitably lose his life in so dangerous an undertaking, consequently he hoped that his Royal Highness would not accede to the request. The result of the interview was that the documents so long waited for were in Bunsen's hands next day!

Although some of the conclusions drawn by Bunsen from his investigations on the composition of the Icelandic rocks are not generally accepted at the present day, yet geologists admit that these researches laid the foundation of modern petrology, and that the original views which he therein expressed mark an era in the history of geological theory. It is now acknowledged that the idea which he was the first to propound, namely, the necessity of examining the chemical composition of eruptive rocks taken as a whole, rather than the determination of their various constituent minerals, must be carried out if we wish to come to an understanding as to their mode of formation. For this purpose, he made an extensive series of complete analyses of the Icelandic rocks. And from these results he drew the remarkable conclusion that in Iceland, and probably in most of the larger volcanic systems, there exist two extreme types of rocks. One of these, richest in silica, is termed the "normal trachyte"; the other, containing less silica and naturally more basic constituents, is the "normal pyroxene." All the Icelandic rocks can be classed as being either one or other of these normal silicates, or as admixtures of the two. In order to account for these well established facts, Bunsen supposed that the two normal types were separated out from the mass of molten silicate in the interior of the earth at distinct points. And he founded this supposition on the fact of the influence of pressure on the melting point (*Pogg. Ann.*, 1850, 81, 562).

This had been independently pointed out by James Thomson, in 1849, as being a corollary of the mechanical theory of heat, and had also been experimentally verified by William Thomson (Lord Kelvin) in the case of water. Bunsen developed this point further by proving that, exposed to a pressure of 156 atmospheres, the temperature of solidification of spermaceti was raised from 47·7°, under ordinary atmospheric pressure, to 50·9°. As volcanic rocks must have been subjected to varying pressures amounting to many thousands of atmospheres, it is clear that the effect of such variation on the point of solidification of the rocks must be very considerable, and that where the pressure

is less the composition of the crystalline mass would be different from that of the rock formed where the pressure is greater. This remarkable theory of the existence of two distinct types of rocks separating out from the same fluid mass, has recently been supplanted by other views, but the facts respecting the composition of the eruptive rocks upon which the idea was based will ever remain, not only a monument to the patience and perseverance of their discoverer, but as some of the most valuable additions to our knowledge of chemical geology.

Bunsen's investigations of the pseudo-volcanic phenomena* of Iceland, and especially those of the great geyser, may, indeed, be considered as models both from a physical and a chemical point of view. The temperature experiments, which were both difficult and dangerous, were conducted by Bunsen in collaboration with Des Cloizeaux. He first shows that the cylindrical shaft, which is no less than 74 feet deep, and 10 feet in diameter, had been built up by the deposition of the silica which the water holds in solution, so that, in Tyndall's words, "the Geyser is the architect of its own tube." Bunsen determined the temperature of the water contained in the tube a few minutes before an eruption, and found that in no part of the tube did the water reach its boiling point. The situation at which the temperature of the water most nearly approached the boiling point under the superincumbent pressure, was about 30 feet from the bottom, reaching there 121·8°, whereas the boiling temperature was 123·8°, making a difference of only 2°. The question occurs, why, under these circumstances, does an eruption take place? This is satisfactorily accounted for by the fact that, owing to the existence at the base of the geyser tube of volcanic vents, through which steam under pressure is passing, the whole column of heated water is lifted, so that whilst originally at a point 30 feet from the bottom the temperature of the water was below the boiling point, when it became raised through a height of 6 feet by the pressure of the issuing steam, its temperature was 1° above the boiling point, the same being true for every point in the cylinder, and thus the ebullition gradually increased until at last it became eruptive. An experimental illustration of Bunsen's geyser theory is described by Tyndall in his well-known work.

The distinct shade of blue possessed by waters of the geyser led Bunsen to examine the colour of distilled water (*Edin. New Phil. Journ.*, 1849, **47**, 95). For this purpose, he enclosed carefully purified distilled water in an horizontal tube 2 metres long, closed by plate-

* An excellent English translation of the memoir "On the intimate connection between the pseudo-volcanic phenomena of Iceland" is found in the volume of *Reports and Memoirs* printed by the Cavendish Society in 1848.

glass ends, the interior of which had been blackened thus showing that the absorptive power of water is exerted less upon the blue than upon the other rays of the spectrum, and explaining the blue colour of certain lakes and rivers, and the colour of sea-water as observed in the Blue Grotto of Capri. The differences in depths of shades of blue possessed by waters in various places are doubtless due to the variation in size of the suspended particles varying in their reflective power.

Of a totally different character was the next piece of work to which I shall refer; it related to the separation of the metals of the platinum group.

In 1868 (*Annalen*, 1868, **146**, 265), Bunsen worked for some time on methods of separating the several metals contained in the residues left after the process of extracting the platinum as practised in the Imperial Mint at St. Petersburg. He fully describes the somewhat complicated processes by which he effected these separations; (1) the elimination of platinum and palladium; (2) the separation of ruthenium; (3) the deposition of iridium and rhodium; and (4) the chief aim of the research, the preparation of pure rhodium and its compounds.

In the course of these experiments, Bunsen met with a singular and unexplained accident, which fortunately had no serious consequences. With reference to this, he writes to me as follows:

"It is still difficult for me to write, as my hands are not quite healed, but I cannot longer delay replying to your sympathetic letter, as I fear you may be uneasy about me. The cause of the explosion is to me still quite inexplicable. I had prepared about a pound of the mixed metals rhodium and iridium by zinc reduction, and had dried the powder at 100° in a water-bath, when, on lightly touching the finely divided metal, which was not quite cold, with my finger, the whole suddenly exploded with the energy of rammed-in gunpowder. This is all the more puzzling, as I have often rubbed a powder of the same metals violently in a mortar in similar quantities without any explosion occurring; I have also heated similar preparations to a redness *in vacuo* without any gas, and certainly without a trace of hydrogen, being evolved. My left hand, with the first finger of which I touched the mass, saved my eyes, as my face and eyes were only superficially burnt by the flames which penetrated through my fingers. My eyes are, with the exception of singed eyebrows and eyelashes, unhurt, and so the explosion will luckily leave behind no serious traces."

In the preceding communication on the platinum metals, Bunsen first describes the well known filter pump which now bears his name.

But in a later publication (*Annalen*, 1868, **148**, 269) he gives further particulars of its construction and use. These are so well known that it is only necessary to say that it is, in fact, a Sprengel's pump in which a column of 28 inches of mercury is replaced by one of 32 feet of water. In this way, a flow of water down a pipe of the above length produces a vacuum perfect up to the limit of tension of the aqueous vapour, and under the diminished pressures thus brought about, all the processes of filtration and of the washing of precipitates can be carried out with much greater rapidity and perfection than is the case when working under the ordinary atmospheric pressure. Here, as in all his published work, Bunsen is precise and exact. To show the time-saving value of the process, he precipitates two equal volumes of chromium sesquichloride solution of known strength by ammonia; the one portion he treats in the ordinary way, the other by the filter-pump method, whereby he demonstrates that, treated by the latter process, the precipitate is completely washed in 1/13th part of the time needed by the old plan, whilst only 1/50th of the volume of wash-water is required. Such filter-pumps, furnished with mercury pressure gauges, are now found in every well fitted laboratory.

A somewhat simpler form of filter-pump, first described by Piccard (*Zeit. anal. Chem.*, 1865, **4**, 45), is, however, now also very generally employed; this consists of a short glass tube attached to the water tap with an inner jet for the water and an outer air-tube, the rapid flow of water carrying down with it a sufficient volume of air—on the principle of the steam injector—to create a diminution of pressure which, although by no means so great as that effected by the filter-pump as described by Bunsen, is still sufficient for many purposes.

As another example of the far-reaching character of his work, a few words must be said about his experiments on the products of the firing of gunpowder.

The nature of the reaction taking place in the firing of gunpowder has attracted the attention of chemists from early years. The accuracy of the simple equation, which at one time was believed to express this reaction was, long ago, rendered doubtful by the observations of Gay-Lussac and Chevreul, but the first exact investigation of the composition, both of the gases and of the solid products of the explosion, we owe to Bunsen and Schischkoff (*Pogg. Ann.*, 1857, **102**, 321). The points of importance which they ascertained were, in the first place, that a large number of salts, whose presence had hitherto not been detected, were shown to be normal constituents of the smoke and solid residue; and, secondly, that many other gaseous products besides carbon dioxide and nitrogen are formed.

The powder was burnt under ordinary pressure, and the maximum

temperature of combustion as well as the maximum pressure were determined. Since 1858, other investigators have taken up this subject, especially Abel and Noble, Berthelot, and Debus.* All these elaborate and more recent researches bear out the conclusion arrived at by Bunsen and Schischkoff, namely, that it is not possible to give any simple expression for the reaction, the products not only being very numerous, but varying considerably in their proportion according to the conditions, especially the pressure, and, therefore, the temperature, under which the explosion takes place.

The invention which perhaps more than any other has popularised the name of Bunsen is that of his celebrated burner.

The Bunsen burner, to the discovery of which I shall refer later on, is not only important from the fact of its almost universal employment, but also because familiarity with its properties led Bunsen to elaborate a series of flame reactions of very wide applicability. In the communication published in 1866 (*Annalen*, 1866, **138**, 257), he showed that the non-luminous flame of the burner could, with advantage, supplant the blow-pipe flame for many analytical purposes. He first describes the constitution of the non-luminous gas flame; next he examines the action of the high temperature of the flame on the emission of light from solid bodies placed in the flame, referring especially to the extraordinary luminous intensity of incandescent erbia, interesting as being the starting point for the enormous industry of the incandescent mantle. He also determines the melting points and the rate of volatility of many salts by means of small beads of material placed at the end of a thin platinum wire in the flame, the rate of volatilisation being ascertained by the microscopic measurement of the diminishing diameters, in given periods of time, of the molten globules. He next details a variety of original and most ingenious methods of detecting minute quantities of the metals and non-metals by the help of reactions effected in the flame. So delicate are some of these methods, as, for instance, that of the detection of gold, that its presence can be with certainty ascertained in one centigram of a sample of a tellurium ore containing only a few tenths of a milligram of the metal.

Another most characteristic contribution to analytical chemistry is the investigation of a method of general applicability, published in 1853 (*Annalen*, **86**, 265), known as the iodometric method and consisting of the volumetric determination of free iodine by means of sulphurous acid, for which has since been substituted the more stable sodium thiosulphate. This method, as every chemist knows, is not only

* To Dr. Debus, one of Bunsen's oldest pupils and friends, I am indebted for particulars of interest connected with Cassel and Marburg.

largely employed in commercial analyses, as, for example, for the estimation of the amount of manganese dioxide in manganese ores and Weldon mud, but it also gives valuable assistance in the determination of interesting theoretical questions, as, for instance, by Bunsen in the separation of cerium and lanthanum, and in the estimation of the atomic weight of the former metal.

Bunsen also devoted much time and labour to the perfection and systematisation of the processes of mineral water analysis.

In 1871, he published a detailed account (*Zeit. anal. Chem.*, 10, 391) of the methods of analysis which he adopted and their results in an investigation, made on behalf of the authorities, which had occupied him for some years, on the chemical and physical properties of the mineral waters occurring in various parts of the Grand Duchy of Baden. These results he afterwards published in pamphlet form. They certainly constitute the most complete series of mineral water analyses existing, and serve as a model in this domain of analytical chemistry. It is interesting to remember that Victor Meyer, who acted at the time as his assistant, carried out a large part of the experimental work.

Having thus pointed out some of the main features of Bunsen's scientific achievements, I now turn to my personal recollections to give you an idea of what manner of man he was, and how he lived and worked.

My reminiscences of Bunsen date as far back as the year 1852. In the autumn of that year, I was introduced to him by Professor von Mohl, the father of the late Frau von Helmholtz, who was then Professor of International Law in the University of Heidelberg. Bunsen had just been called from Breslau to fill the Chair of Chemistry at Heidelberg in succession to Leopold Gmelin, best known to English chemists as the author of the great handbook translated by our late editor, Henry Watts, and published by the Cavendish Society. I shall never forget the first sight of the man who afterwards became one of my most intimate and valued friends, and to whom I owe more than I can tell. At that time, Bunsen was at the height of his powers, physical and mental; he stood fully six feet high, his figure was well knit and powerful, his manner was one of suave dignity, whilst his expression was that of great kindliness and of rare intelligence. Nor did this first impression of his bearing and character ever change, much less lose force. On the contrary, the more intimate became my knowledge, the more had I cause to respect and admire him. His was a heart free from guile, guiding a temper equable and amiable. During my long and intimate friendship, I never heard him set down aught in malice, or express more than a mild and good-natured

remonstrance, as when, for instance, one of the "practicanten" had adopted some faulty method of analysis, the master would remark: "Mein Gott, wie konnten Sie so was thun!" His genial, yet quietly dignified, manner placed strangers at their ease, at once inspiring confidence and commanding respect. All saw in him a man worthy of esteem and safe to trust, whilst those who were favoured by his more intimate friendship knew that for true modesty and greatness of heart he was excelled by none; they feel that for them he was the "chevalier sans peur et sans reproche," and that his companionship, whether scientific or social, was something to be proud of, the recollection of which remains as one of the most fruitful as well as one of the pleasantest of their lives.

Considerate and generous towards the opinions of others, he held firmly to his own, which at times he did not fail strongly to express. Simple and straightforward, he disliked assumption and hated duplicity; single-minded and wholly devoted to his science, he abhored vanity and despised popularity-hunting. Indeed, of so retiring a disposition was he, that it was difficult to get him to take part in public proceedings, and next to impossible to induce him to make any public utterance of either a scientific or of a social character.

Another and a remarkable trait in his character was his keen sense of humour. This gave a charm and a zest to his society greatly appreciated by his friends, but of all his witty sayings which passed from mouth to mouth as "Bunsen's last," none was ever tinged with ill-nature, for this was foreign to his whole being. A large and interesting collection of these "Bunseniana" might be made. Suffice it here to mention a few. When travelling with Kirchhoff and myself in England during the autumn of 1862, Bunsen was mistaken by a lady for his distant cousin, "the Chevalier" Bunsen. "Did you ever complete, sir, your great work on 'God in History'?" asked the lady. "Alas, no," replied Bunsen, "my untimely death prevented me from accomplishing my design." One of his assistants, engaged in rearranging the collection of specimens, came to him with a bottle containing quinine, and wishing to find out whether the Geheimerath remembered the formula for the alkaloid, asked him for it; Bunsen, who was, however, not to be caught by chaff, replied, "Wozu denn, Herr Doctor, sind die Handbücher?" Like many men who are engrossed in their special calling, Bunsen was often absent-minded, and many good stories were current about the mistakes which he thus unwittingly made. He had a well known difficulty in remembering names; one day a visitor called who he knew quite well was either Strecker or Kekulé. During the conversation he was endeavouring without success to make up his mind which of these two gentlemen was his caller. First he thought it was Kekulé, then he convinced himself that he was talking to Strecker. At last, however, he decided

that it was really Kekulé. So when his visitor rose to take leave, Bunsen, feeling confidence in his latest conclusion, could not refrain from remarking, "Do you know that for a moment I took you for Strecker!" "So I am," replied his visitor in amazement.

His, too, was a most affectionate nature, and one may regret that this side of his character was never freely called forth by family life. For Bunsen, like Dalton, tried to explain this failing by saying that he could never find time to get married. And this loneliness, especially in later life, oppressed him, and he often felt his isolated position keenly. When bidding him good-bye after my summer visits to him, he would smile sadly and remark, "Jetz verlassen Sie mich wieder in meiner Einsamkeit." The following extract, from a letter to myself, referring to a notice of his life and labours, which appeared with a portrait, in 1881, in the columns of *Nature*, indicates more clearly than any words of mine can do, this side of Bunsen's character:

"The kind things you say of me in *Nature* touch me the more, as I see in them the faithful expression of your old true friendship for me, which is one of the great joys of my old age. When one arrives, as I shall do in a few days, at one's seventieth birthday, one has only to live through a short span of bodily and mental decay. Standing as I do at that period of my life, I feel as keenly as ever how modest and contemptibly small is the amount which I have added to the building of science. In the years which I am rapidly approaching, one lives more in the recollection of past happy days than in the present; and to the most pleasure-giving of them belong those which for many years we spent in true friendship together."

As another touching illustration of his affectionate disposition, I may mention that when congratulated one day by a friend on his having received some high mark of distinction, he remarked, "Ah, the only value such things had for me was that they pleased my mother, and she is now dead!"

It may here be well to mention that, in the year 1881, a congratulatory address, accompanying a bronze statuette of Berzelius, from his old pupils, was presented to Bunsen on the occasion of the celebration of the jubilee of his doctorate.

A letter written to me on Nov. 3 in that year indicates the feelings of regard and affection which bound together the Professor and his students.

"My very dear Friend,

"Please accept my most hearty thanks for all the kindness you have shown towards me on this occasion, which has been so exciting for me. Of all the friendly interest that has been shown, what gave me the greatest and most heartfelt pleasure were the con-

gratulations to which your signature bore witness, amongst those of so many old friends, and of the donors of the beautiful and artistic gift which I received from the hands of Baeyer on the fiftieth anniversary of my graduation.

"I and all friends will be glad to see you. I was absent from here on my anniversary day, hoping in that way to escape all official notice, but on my return I found so many tokens of kind interest that I scarcely see how it will be possible for me to answer each one separately . . . , and so I am beginning to feel very much exhausted after all I have been through; I long most heartily for your friendly visit, which will be the best medicine for me."

This flight of the principal actor in the scene is very characteristic of the man, and *à propos* of this Kopp writes to me in January 1882:

"We had expected you to be present at the Jubilee. Bunsen had secreted himself with a few intimate friends in Gugenheim on the Bergstrasse, he had noted the locality of his retirement on a card, which, in case of your arrival, my wife was privately to hand to you. Bunsen took the unavoidable in good part, and not wholly without pleasure. He is very fresh and well, apart from his nearly permanent bronchial catarrh; he grumbles much, and is therefore perfectly normal."

In 1887, the seventh centenary of the foundation of Heidelberg University was auspiciously celebrated. Bunsen invited me to be his guest during the ceremony. During the inaugural discourse by Kuno Fischer, which lasted more than three hours, Bunsen fell asleep, as well he might do, but a more than usually eloquent passage disturbed his rest, and he woke up with a start, and whispered to me: "I thought I had dropped a test-tube full of rubidium on to the floor!"

Nothing was more distasteful to him than the etiquette of the Court. Nevertheless, during these festivities at which the Grand Duke of Baden, the Prince of Prussia, and other magnificos were, of course, present, Bunsen became the cynosure of neighbouring eyes. The recipient of heaps of Orders of all kinds, from all quarters, he never exhibited them except when he went to Court, or was invited to meet his Sovereign. To be used on such occasions only, he kept an "Order" coat, a 'Frack' or tail coat, upon the breast of which he had stitched as many of the stars and crosses as it would comfortably hold. During the Jubilee, the Grand Duke held a Court in the castle, and presentations were made. Bunsen, who had already paid his *devoirs* to the Grand Duke's party, expressed his unwillingness again to go through the necessary formalities, but, after some persuasion on my part, he consented, hoping, as he said, to conceal himself

behind the crowd of officials and dignitaries of all sorts who thronged the hall in which the Royalties were assembled. So we walked together up to the castle, in evening dress, as the custom is, Bunsen wearing his 'Orders.' The streets through which the procession of magnates was to pass were filled to overflowing by a good-natured crowd, no military or even police being present to clear the way, so as the royal carriages came up the steep road leading to the castle, a block occurred, and, as luck would have it, that containing the Grand Duke, the Duchess, and the Prince of Prussia came to a standstill at the exact point where Bunsen and I stood endeavouring to make our way through the crowd. The Duke at once recognised the Geheimerath, and beckoned him to come to the carriage, and there and then they had a friendly chat, and I had the honour of being presented. As soon as the cortège moved on, I had a good laugh at Bunsen, who, endeavouring to escape from all notice and attention, was entrapped in this amusing fashion.

Let me next endeavour to give you a picture of the master working in his laboratory.

When he first came to Heidelberg in the summer of 1852, Bunsen found himself installed in Gmelin's old laboratory. This was situated in the buildings of an ancient monastery, and there we all worked. It was roomy enough; the old refectory was the main laboratory, the chapel was divided into two, one half became the lecture-room and the other a storehouse and museum. Soon the number of students increased and further extensions were needed, so the cloisters were enclosed by windows and working benches placed below them. Beneath the stone floor at our feet slept the dead monks, and on their tombstones we threw our waste precipitates! There was no gas in Heidelberg in those days; nor any town's water supply. We worked with Berzelius's spirit lamps, made our combustions with charcoal, boiled down our wash-waters from our silicate analyses in large glass globes over charcoal fires, and went for water to the pump in the yard. Nevertheless, with all these so-called drawbacks, we were able to work easily and accurately. To work with Bunsen was a real pleasure. Entirely devoted to his students, as they were to him, he spent all day in the laboratory, showing them with his own hands how best to carry out the various operations in which they were engaged. You would find him with one man showing the new method of washing precipitates so as to save time and labour, or with another working out a calibration table of a eudiometer, or with a third pointing out that the ordinary method of separating iron from aluminium is unsatisfactory and carrying out a more perfect process before his eyes. Often you would find him seated at the table

blow-pipe—the flame in those days was fed with oil—making some new piece of glass apparatus, for he was an expert glass blower, and enjoyed showing the men how to seal platinum wires into the eudiometers, or to blow bulb-tubes for his iodometric analyses. Maxwell Simpson, who worked with Bunsen in the fifties, tells me that one day he saw Bunsen blow a complicated piece of glass apparatus for a pupil, who quickly broke it; Bunsen then made him a second, which at once met with a similar fate; without a murmur, Bunsen again sat down to the blow-pipe and for the third time presented the student (who we will trust looked ashamed of himself) with the perfect apparatus. Then he would spend half the morning in the gas-analysis room, going through all the detailed manipulation of the exact measurement of gaseous volumes, and showing a couple of men how to estimate the various constituents of a sample of coal-gas, and pointing out the methods of calculating the results, and then leaving them to repeat the processes from beginning to end for themselves.

His manipulative ability was remarkable; his hands, though large and powerful, were supple and dexterous. He was amusingly proud of having a large thumb, by means of which he was able to close the open end of a long eudiometer filled with mercury and immerse it in the mercury-bath without admitting the least bubble of air, a feat which those endowed with smaller digits were unable to accomplish. Then he had a very salamander-like power of handling hot glass tubes, and often at the blow-pipe have I smelt burnt Bunsen, and seen his fingers smoke! Then he would quickly reduce their temperature by pressing the lobe of his right ear between his heated thumb and forefinger, turning his head to one with a smile as the "agony abated," whilst it used to be a joke amongst the students that the master never needed a pincette to take off the lid from a hot porcelain crucible.

Accuracy of work was the first essential with him—most of us learnt for the first time what this meant. Six weeks' work was spent on a single silicate analysis, but most of us contrived to keep two such analyses going at once, whilst an analysis of coal-gas occupied a week or ten days. Not that he was averse to quick processes, indeed many of his own investigations contain novel proposals for shortening chemical methods, but this was never done at the expense of accuracy.

After having learnt his methods of quantitative work, of silicate analysis, for example, and after having gone through a course of gas analysis, those of us who had already been more or less trained elsewhere, were set upon some original investigation. Lothar Meyer, who worked at the next bench to myself, being a medical student, was set to pump out and analyse the blood-gases; Pauli and Carius worked on gas-absorption, employing for this purpose Bunsen's recently in-

vented absorptiometer; Russell was set to work out a new method of sulphur determination in organic bodies; Matthiessen was put on to the electrolytic preparation of calcium and strontium; Schischkoff analysed the gaseous products of gunpowder fired under varying conditions; Landolt had to find out the composition of the gases in various portions of a flame, and I worked by myself in one of the monks' cells upstairs on the solubility in water of chlorine when mixed with hydrogen and carbonic acid, the object being to ascertain whether this gas obeys the law of Dalton and Henry.

These are only some of the investigations on a variety of subjects carried on in the old monastery by Bunsen's pupils under his supervision, and they indicate only a tithe of his activity; for at the same time he was engaged in investigations of his own—he always had two or three on hand at once.

When Bunsen accepted the Chair of Chemistry at Heidelberg, the Baden Government agreed to build him a new laboratory. This was accordingly done, the plans having been worked out by him to the smallest detail, and in the summer of 1855 the new laboratory in the Plöck Strasse was opened. The rooms were by no means so lofty as those of our more modern laboratories, and as students from all parts of the world streamed in in large and increasing numbers, the new building soon became inconveniently crowded, and many applications for working benches had to be refused.

Some short time before the opening of the new laboratory, the town of Heidelberg was for the first time lighted with gas, and Bunsen had to consider what kind of gas-burner he would use for laboratory purposes. Returning from my Easter vacation in London, I brought back with me an Argand burner with copper chimney and wire-gauze top, which was the form commonly used in English laboratories at that time for working with a smokeless flame. This arrangement did not please Bunsen in the very least; the flame was flickering, it was too large, and the gas was so much diluted with air that the flame-temperature was greatly depressed. He would make a burner in which the mixture of gas and air would burn at the top of the tube without any gauze whatsoever, giving a steady, small, and hot, non-luminous flame under conditions such that it not only would burn without striking down when the gas supply was turned on full, but also when the supply was diminished until only a minute flame was left. This was a difficult, some thought it an impossible, problem to solve, but after many fruitless attempts, and many tedious trials, he succeeded, and the "Bunsen burner" came to light. On the theory of the "Bunsen burner" I need not detain you, for it has already been brought before the Society in his usually clear and masterly manner by our President (this Journal,

1877, i, 31, 627). I may, however, here remark that so general, indeed so universal, has the use of this become that its name and value must be known to, and appreciated by, millions of the human race. Yet how few of these have any further ideas connected with the name of its author.

Another discovery which early brought him prominently before the public was that of the "Bunsen," or as he preferred to call it, the "carbon-zinc" battery, a description of which has already been given. The manufacture of either the battery or the burner might, had the inventor wished, have been so guarded as to bring in a large fortune. But Bunsen had no monetary ambition, although he fully appreciated the importance of applied science, and this is a fine trait in his character. He not only disliked anything savouring of money-making out of pure science, but he could not understand how a man professing to follow science could allow his attention to be thus diverted from pure research. "There are two distinct classes of men," he used to say, "first those who work at enlarging the boundaries of knowledge, and, secondly, those who apply that knowledge to useful ends." Bunsen chose the first—perhaps one may say the higher—part, and the notion of making money out of his discoveries, or of patenting any of them, never entered into his head. As illustrating this habit of mind, I remember that once we were talking about a former pupil of his, of whose scientific ability he entertained a high opinion. "Do you know," he remarked to me, "I cannot make that man out; he has certainly much scientific talent, and yet he thinks of nothing but money-making, and I am told that he has already amassed a large fortune. Is it not a singular case?" To which I replied that I did not find it so very remarkable!

In the new laboratory, research work was carried on with even greater activity than it had been in the old one. My own work on photochemical measurements was first carried out in a darkened chamber under the slates, where the summer temperature was usually above blood-heat, and afterwards in Bunsen's private room downstairs. Men whose names have long ago been household words with us came to work under the Master. Baeyer carried out his early work under Bunsen's care, though after a time he left to work with Kekulé, who had just set up a private laboratory in the neighbourhood. Lothar Meyer, Carius, and Landolt were continuing their several researches; Dexter worked on the atomic weight of antimony, Holtzmann on the cerium metals, whilst Pebal, Erlenmeyer, Meidinger, Lieben, Barth, Moritz Hermann, and Lotz each published interesting communications; and Bahr from Stockholm, Frapolli from Milan, Pavesi from Padua, and Lourenço from Goa were also occupied

in research. Most of this work Bunsen had initiated, all he assisted by co-operation and advice.* Then, in addition, there were the beginners, to the number of 60 or 70, all of whom were looked after by the Professor and with some of whom he would spend hours showing them how to detect traces of metals by aid of the "flame reactions," or how to estimate the percentage of dioxide in pyrolusite by his iodometric method. So from Bunsen all who had eyes to see and ears to hear might learn the important lesson that to found, or to carry on successfully, a school of chemistry the professor must work with, and alongside, of the pupil, and that for him to delegate that duty to an assistant, however able, is a grave error.

How, it may be asked, could a man who thus devoted himself to supervising the work of others in the laboratory—and who, besides, had a lecture to deliver every day, and much university business to transact—how could he possibly find time to carry out experimental work of his own? For it is to be noted that Bunsen never kept an assistant to work at his researches, and unless co-operating with someone else, did all the new experimental work with his own hands.

It is true that in certain instances he incorporated the results of analyses, made by a student whom he could trust, into his own memoirs; notably this was the case with the silicate analyses which he used in his chemico-geological papers, and with many of the examples given in illustration of some of his new analytical methods. Then, spending the whole day in the laboratory, he was often able to find a spare hour to devote to his own work, of devising and testing some new form of apparatus, of separating some of the rare earth metals, or of determining the crystalline form of a series of salts.

Again the editing of the research, and the calculations, often complicated, which that involved, were carried on in the early morning hours. When, for four summers after the year 1857 I spent my vacations working at Heidelberg, I lived in his house, and although I rose betimes, I always found him at his desk, having begun work often before dawn.

Then, although he frequently travelled during the vacations at Easter and in the autumn, often, I am glad to remember, with myself as companion, he generally returned after a short absence to continue

* During the twenty years following 1856 the following were amongst those who worked with Bunsen: Graebe, Ladenburg, Bütschli, Wichelhaus, Laspeyres, Richard Meyer, Victor Meyer, Crum Brown, Thorpe, H. Rosenbusch, Horstmann, Emmerling, A. Salkowski, Bunte, Guido Goldschmiedt, Gibson, Smithells, Michael, Zorn, Bernthsen, Königs, Treadwell, Herzig, Fabinyi, Wanklyn, Phipson Beale, Cartmell, Long, Schischkoff, Andrejeff, Beilstein, Filipuzzi, Schneider, Dollfus-Ausset, Kündig, Goppelsroeder, Mayboom, Nessler, Winckler, Rose, Lucius, Friedländer, L. Mond, Sprengel, Messel, and lastly, Curtius, who at present occupies the Chair of Chemistry at Heidelberg.

an unfinished, or to commence some new, research, and during these quiet days much work was done by both of us.

I will now say a few words about Bunsen as a lecturer.

Bunsen lectured on general chemistry every morning in the week from 8 to 9 in the summer, and from 9 to 10 in the winter semester. The lectures were interesting and instructive, not from any striving after oratorical effect, or by any display of "firework" experiments, but from the originality of both matter and illustration. His exposition was clear, and his delivery easy, and every point upon which he touched was treated in an original fashion; no book, of course, was used or referred to; indeed, he avoided much consultation of handbooks, the only two which I have seen him occasionally turn to for the purpose of looking up some facts about which he had doubts were "Gmelin" and "Roscoe and Schorlemmer." When occasionally one of the 'Practicanten' consulted him about a passage in some manual which appeared defective, he would laughingly remark that most of what is written in books is wrong.

The illustrative lecture experiments, which he invariably performed himself, were generally made on a small scale, were often new, always strictly relevant to the matter in hand, and never introduced for mere sensational effect. He paid much attention to these experiments, and after the table had been set in order for the particular lecture by the assistant, he would regularly spend half-an-hour, sometimes an hour, in convincing himself that all was in readiness and in rehearsing any experiment about the success of which he was not perfectly certain.

He used few notes, but it was his habit to write up any numerical data in small figures on the blackboard, and to refresh his memory with these when needed. When I attended the lectures in the early fifties, Bunsen used the notation and nomenclature of Berzelius, writing water $\dot{H}$, and alumina $\dddot{Al}_2$. Later on, he still employed the dualistic notation, writing $KOSO_3$, $HOSO_3$, for K_2SO_4 and H_2SO_4, indeed, I believe that he never adopted our modern formulæ or used Cannizzaro's atomic weights, although his determination of the atomic heat of indium and his work on cæsium and rubidium were amongst the most important contributions towards the settlement of those weights.

Bunsen did not enlarge in his lectures on theoretical questions, indeed to discuss points of theory was not his habit and not much to his liking. His mind was eminently practical; he often used to say that one chemical fact properly established was worth more than all the theories one could invent. And yet he did much to establish the evidence upon which our modern theories rest.

On this point, the following statement, for which I am indebted to Dr. Gibson, who worked with Bunsen from 1873 to 1875, is of interest: "What was impressed" in Bunsen's lectures, "was not so much the theories concerning the elements and their compounds as the salient facts. The properties and behaviour of the elements were described with a clearness and wealth of experimental illustration that made their individuality and characteristics stand out in prominent relief compared with which such things as theories and formulæ were almost lost sight of. At a very early stage of the course, the greater part of two lectures was devoted to an analysis of mercuric oxide carried out before the class in the most precise and painstaking manner. The whole was a masterly exposition of analytical method involving a detailed but most lucid discussion of the various sources of error and of the two ways by which accuracy may be arrived at, namely, either by reducing these errors to a minimum or by estimating them and making the necessary corrections."

Concerning this side of Bunsen's character, and on the influence exerted by his work on chemical theory, I cannot do better than quote the judgment of Cannizzaro, who, in his eloquent *éloge*, uses the following words:

"Bunsen did not take any active part in the theoretical discussions which took place during that period of his scientific career, but he was not indifferent to the fundamental arguments of chemical science, that is, the atomic weights of the elements and the formulæ of their compounds. Whilst controversy raged, he was silently employed in collecting experimental data, and teaching how these can be best obtained in order to settle all pending questions. This was his true mission. And this he fulfilled admirably."

To this passage, Cannizzarro appends a note which is so characteristic both of the writer and of his subject that I venture to quote it:

"In 1860, whilst I was on my way to attend the Chemical Congress at Carlsruhe, which was convened in the September of that year by Weltzien, Wurtz, and Kekulé, I stayed for several days at Heidelberg, where I had an opportunity of discussing with Bunsen the questions which were to be raised at the Congress, namely, the choice of a system of atomic weights of the elements, and of the notation of their compounds. I found him well informed as to my published views on these subjects, which he had discussed with his intimate friend Kopp. He was satisfied with the attempt to effect an agreement between the conclusions drawn from atomic heat, isomorphism, and from the application of Avogadro's theory, but he did not enter seriously into the discussion, and in conversation on the subject he immediately reverted to an enumeration of the new experiments which ought to be made in order to settle doubtful points."

À propos of Bunsen's lectures, I may here relate a story which is characteristic of the man.

Although the motto of "Lehr-und Lern-Freiheit" is that of every German University, yet it is obligatory on all candidates for public appointments to bring up certificates, signed by the Professor, of attendance on specified lectures. Bunsen, considering this a matter of form, usually signed "mit ausgezeichnetem Fleiss," without further inquiry. On one occasion, however, looking at the applicant, he remarked, "Aber Herr Dingskirch ich habe Sie in die Vorlesung gar nicht gesehen." "Ja, Herr Geheimerath," replied the student, "ich sitze aber immer hinter die Pfeile." "Ach da sitzen so viele," was the only remark vouchsafed by the Geheimerath, who at once filled in the schedule, "mit ausgezeichnetem Fleiss!"

In conclusion, I may remark that Bunsen's constitution was a vigorous one, and it carried him fairly well through a long life; still, continuous exposure to the fumes and vitiated air of the laboratory induced bronchial troubles, from which in later life he suffered considerably. Beyond one sharp attack of peritonitis when travelling with Pagenstecher in the Balearic Islands, I do not think he ever had a serious illness. His habits were frugal, the only extravagance in which he indulged being his cigars. Of these he consumed a fairly large number, always having one or a part of one in his mouth; but as he generally allowed it to go out many times before he finished smoking it, the time it lasted was much above that of the average smoker.

Although taking no active part in German politics, Bunsen was a staunch Liberal; and no one rejoiced more than he on the consummation of the unification of the German people under the headship of the Emperor William. He was, however, no admirer of Bismarck's *régime*. On Mitscherlich's death, Bunsen received a very pressing invitation to become Mitscherlich's successor in Berlin. On this subject, he writes to me: "Very liberal offers with regard to Mitscherlich's professorhip have been made to me, but I have declined them, as I did not wish to belong to the regiment of Herr von Bismarck, or to start again from the beginning with chemistry, the position of which had there fallen so low. In addition to that, they have here complied with the wishes which I had before expressed, and have offered Kopp a professorship here, besides raising the fund of my institute by a thousand gulden."

In 1889, Bunsen retired from active University life, resigning his professorship, and therefore his official residence, and retiring to a pretty little villa in "Bunsen Strasse" which he had purchased, where he spent the remainder of his days in quiet repose. His chief relaxation and enjoyment throughout his life in Heidelberg was to

wander with Kirchhoff or Helmholtz or some other of his intimate friends through the chestnut woods which cover the hills at the foot of which the town lies. As the infirmities of age increased and his walking powers diminished, he was obliged to take to driving through the woods along the charming roads which intersect the hills in all directions. Writing became a difficulty, and in his latter days the news of him came to me through our mutual friends Quincke and Königsberger. One of the last letters I received from him is dated June 4, 1890:

". . . . I have been suffering for weeks from the after-effects of influenza, and I am still so weak that I have to spend my days on the sofa, and have scarcely strength to walk the few yards to dinner at the Grand Hotel. When I think that next March I enter on my eightieth year, I must resign myself to the fact that such a state of things is inevitable. My hearing, too, becomes more and more difficult and my eyes are worse, so I have to deny myself all social intercourse, and only see now and then one of my old friends who comes to look me up. But in spite of all this, I can still feel the humour of life. This is, unfortunately, not the case with Kopp, who has just resigned his chair. He suffers constantly, but with his chronic hypochondriacal temperament he was unable to fulfil his professorial duties and feels very unhappy. I hope that in time he will resign himself to the inevitable. . . . "

Few men knew Bunsen so well, or admired him so much as Leo Königsberger, the distinguished professor of mathematics at Heidelberg. The following appreciative remarks contained in a letter to myself on Bunsen's mental constitution seem to me so true that I make no apology for here quoting them:

"Bunsen did not possess a mathematical brain in the sense so splendidly illustrated in the cases of Maxwell and Kelvin. He had, however, a logical mind, enjoying the rational analysis of recognised truths, and was thus able, thanks to the wonderful intuitive power of a great scientific man, and thanks also to his æsthetic character, to grasp and to understand rather than to explain phenomena. These, therefore, were rendered evident to him, not so much by an exact intellectual process, as by the evidence of the senses and by the gratification which their perception afforded. Quite otherwise was it with Kirchhoff, as he entered frequently and with zest even into unfruitful mathematical or philosophical speculations. It was always interesting to listen to these two remarkable men dispute about some mathematical, scientific, or philosophical subject. Still more interesting was it, however, to watch, when he was present, the incomparable Helmholtz looking silently on, from his calm Olympian heights, with an appreciative but meaning smile as the discussion proceeded."

But although Bunsen was not a mathematician as compared with the men mentioned above he not only possessed great mathematical ability, but what is more important, the power to apply mathematical treatment to chemical problems. He constantly pressed upon all his pupils the necessity for a chemist of a thorough training in mathematics and physics; indeed, I have heard him exclaim, "Ein Chemiker der kein Physiker ist, ist gar nichts."

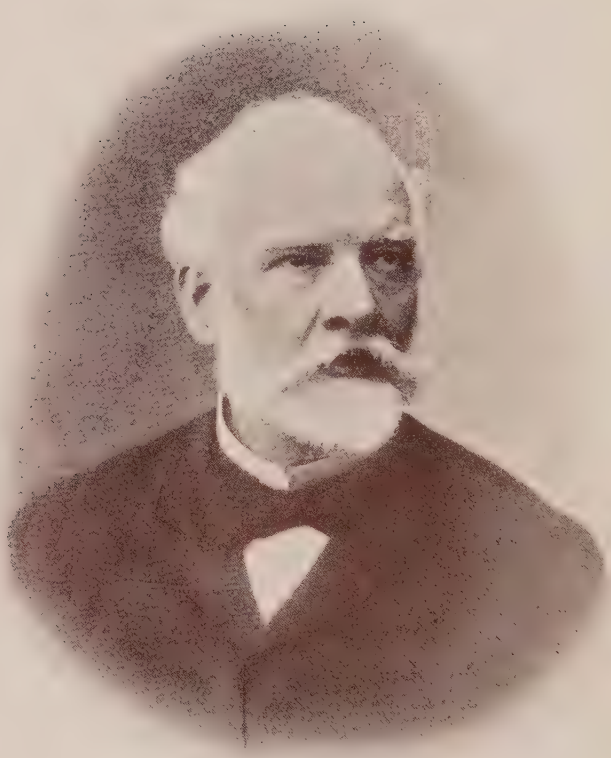
Bunsen at the time of his death had been for many years our senior Foreign Member, having been elected on February 1, 1842, during the first session of our Society. It was not till 1858 that he became a Foreign Fellow of the Royal Society. In 1860, the Copley medal was awarded to him, and in 1877 he and Kirchhoff were presented with the Davy medal, being the first occasion of its award, in recognition of their researches and discoveries in spectrum analysis.

With respect to the award of the Davy medal, Bunsen writes to me on Nov. 10, 1877, as follows: "My best thanks for your friendly letter with the news of the very unexpected distinction which has been conferred upon me. I received it almost simultaneously with the official announcement from Williamson, and I am indeed quite confused by so much kindness from my English friends."

Another English honour conferred upon him was that of the award in 1898 of the Albert medal of the Society of Arts given for "distinguished merit in promoting art, manufacture, or commerce," in recognition of his numerous and most valuable applications of chemistry and physics to the arts and to manufactures.

Almost up to the last Bunsen continued to take a vivid interest in the progress of scientific discovery, and though suffering from pain and weakness, ever preserved the equanimity which was one of his lifelong characteristics. Three days before his death, so Quincke writes to me, he lay in a peaceful slumber, his countenance exhibiting the fine intellectual expression of his best and brightest days. Thus passed away, full of days, and full of honours, a man equally beloved for his great qualities of heart as he is honoured for those of his fertile brain, the memory of whom will always remain green amongst all who were fortunate enough to number him amongst their friends.

[Before commencing the Lecture, Sir Henry Roscoe read the following telegram from Dr. Philipp Bunsen of Marburg, the nephew and executor of the late Professor. "On the occasion of the Memorial Lecture, the Bunsen family joins sincerely with the illustrious Society and sends respectful thanks and compliments."]



C. Friedel

FRIEDEL MEMORIAL LECTURE.

By J. M. Crafts, Professor.

The tomb of Friedel at Montauban bears the inscription :

Charles Friedel
né à Strasbourg le 12 Mars 1832
décédé à Montauban le 20 Avril 1899.
Membre de l'Institut.

"Le juste vivra par la foi
La mémoire du juste sera en bénédiction."

So far as a tombstone can bear faithful witness to a life, this short description is true of a man who chose science for his occupation, and strove to do his duty towards God and man with keen observation of things temporal and a simple faith in things eternal.

We, as members of the Chemical Society, are chiefly concerned with his contributions to science, but enumeration of these will not be complete unless it is said that high among his contributions to the advancement of science stands the influence of a very beautiful character and of a well-balanced judgment upon the men of his time, even extending beyond his own nation, and during the excited period after the French national disaster, serving as a connecting link between the scientific reasoning of his countrymen and the spread of philosophy abroad.

The influence of individuals and of schools upon the patronage of the younger men for educational positions is peculiarly important in France. The destiny of a student of science depends greatly upon the leader whom he chooses to follow, and there is sufficient cohesion among the members of a school to make it an effective body. That founded by Wurtz was continued by Friedel, who was the oldest of the French followers of Wurtz, and only fifteen years younger than his leader. His immediate associates were Gautier, Grimaux, Salet, Lebel, and, later, Hanriot and the Combes. With Friedel, as with Wurtz, charm of character, as well as scientific talent, contributed to enlarge this group of men, bound together by a common regard and by community of views, until the school became an important factor in the nation's progress.

One of the most notable channels through which scientific patronage is exercised is in the Academy of Science, whose organisation offers very effective means of exerting influence in the election of new members, in the appointment to professional places, in the annual distribu-

tion of large numbers of prizes, and in the examination by committees of questions of scientific, and sometimes of national, interest. Friedel played an important part in this work, and his competency in chemistry, mineralogy, and mathematics, together with his evident fair-mindedness, gave great weight to his opinion among his colleagues.

There is much significance in the way in which the title, Member of the Institute, is used as the only record of occupation placed upon Friedel's gravestone, and it is quite in accord with French usage to consider this distinction one of the highest that the nation can bestow; thus Napoleon, in familiar letters, having nothing to do with science, signs himself, "Bonaparte, Général en Chef, Membre de l'Institut."

The circumstances of Friedel's family, as well as his subsequent position, favoured the development of his scientific career. His childhood, passed at Strasbourg, brought him, even during school years, in contact with men of science, and his inclination for scientific studies was favoured by his parents.

He took his Bachelor's degree in letters in 1849, and that in science in 1850. He then entered his father's counting-house, and while there had an opportunity of attending lectures by Pasteur, Daubrée, Bertin, and Lereboullet at Strasbourg University. His stay in the counting-house lasted only a year, and, as might have been expected, the attractions of science presented by such men drew him away from commerce.

In 1851, he went to Paris to live with his maternal grandfather, G. L. Duvernoy, Professor at the Collége de France and the Museum of Natural History. He took the Licentiate degree in mathematics at the Sorbonne in 1854, and that in physical science July 7th, 1855. While pursuing these studies, he commenced research work at the Museum, and a letter, dated December 21st, 1854, speaks of the discovery of two new faces in crystals of corundum, given him for examination by Dufrénoy (he had refused a place of assistant with that mineralogist), and also of a research confided to him by Wurtz.

He followed the lectures of Senarmont at the School of Mines, and formed a strong personal attachment to him while engaged in mineralogical studies under his guidance. In 1856, Friedel was appointed Curator of the mineralogical collection of the School of Mines, then under the direction of Dufrénoy, and for the remainder of his life was actively occupied with enriching that important collection. He was at first attracted by the crystallographical side of mineralogy, and then towards optics, until, at the suggestion of Senarmont, he thought of devoting himself to mathematics and becoming an astronomer; but soon the chemical side absorbed his attention, and during the remainder of his life his time was divided between pure chemistry

and chemical mineralogy, although he always took especial pleasure in the examination of crystalline forms. Somewhat later, he was advised by Pasteur to seek an entrance to the Academy of Science in the section of mineralogy, to which Pasteur himself belonged, but Friedel preferred to make chemistry his principal study.

On November 10th, 1854, Friedel entered Wurtz's laboratory, and soon became its most distinguished pupil. There were some sixteen places, of which usually one-third were occupied by foreigners, particularly Russians, Germans, Austrians, and Italians. The rooms at the School of Medicine were inconvenient, having been designed for other purposes, and the balances were placed in an anatomical lecture room; yet this school succeeded in some measure to that of Liebig, and was visited by chemists of all nations; for European science still held to the traditions of the time of Humboldt, and a sojourn, however short, at Paris was considered a desirable part of a scientific education.

Friedel's researches upon acetones and aldehydes were made at this time, 1857—1863, in the laboratory of the School of Medicine, and his views of their constitution, and his discovery of secondary propylic alcohol, were immediately recognised as important contributions to chemical science.

In 1866, the privilege of a small laboratory at the School of Mines was attached to the place of Curator of the mineralogical collection, and it was there that Friedel's work in mineralogy was done, as well as the researches upon silicon compounds and the aluminium chloride reaction. He had, between 1866 and 1880, an apartment in the buildings of the School of Mines. In 1869, he took his Doctorate degree, offering two theses, one upon acetones and aldehydes, and the other upon the pyroelectric properties of crystals. In 1871, he gave the lectures in mineralogy at the Normal School (Ecole normale supérieure), replacing Des Cloizeaux.

In 1876, he was appointed Professor of Mineralogy at the Sorbonne, succeeding Delafosse, and he there organised a laboratory for mineralogy. Two years later, he was chosen Member of the Academy of Science in the chemical section, filling the place left vacant by the death of Regnault.

The death of Wurtz in 1884 left Friedel the oldest representative of Wurtz's school and he succeeded to Wurtz's professorship of organic chemistry at the Sorbonne, exchanging this chair for that of mineralogy. The laboratory accommodation for chemical students was very insufficient at Paris and the old buildings at the Sorbonne were still more unsuited to such work than were those of the School of Medicine. A project for new and greatly enlarged buildings was under consideration, but with small prospect of immediate realisation, so that Friedel devoted his energy to the construction of a temporary

laboratory building beyond the Luxembourg Garden in the Rue Michelet, where also the inorganic laboratories of the Sorbonne under Troost were located. These rooms, although lacking the luxury of the modern laboratory, proved to be convenient and the places for about fourteen students were always filled.

In January, 1895, the new laboratories at the Sorbonne, built upon Friedel's plans, were opened with places for thirty students in organic chemistry, and at the same time he organised a three years' course of lectures and laboratory instruction in industrial chemistry at the provisional laboratories in the Rue Michelet. Such instruction had heretofore been wanting in Paris. It was undertaken at Friedel's instigation by the Municipal Government, and the attention required by the initial steps, and afterwards by the direction of this new course, formed an important occupation during the last four years of his life.

He took the chief part in 1899 in founding the Revue Générale de Chemie pure et appliquée, which is largely devoted to industrial applications. Friedel was associated with Wurtz in editing the Dictionaire de Chemie pure et appliquée and after Wurtz's death in 1884 became the chief editor of the supplements, of which the second has only progressed to the letter G. During the later years of his life, editorial work, together with the work upon committees and administrative duties, engrossed more and more of his time, and he often regretfully looked back upon the hours spent upon experiments in his laboratory which he ever considered the most enjoyable.

He was one of the founders of the French Chemical Society, four times its President, and a constant attendant at its sittings. He took the initiative in founding the French Society for the advancement of Science in 1885, and presided at the meeting at Nancy in 1886. He presided at the International Congress of Chemists held in 1892 at Geneva for the reform of the nomenclature of the fatty acid series, and up to the time of his death was occupied with the arrangement of a similar meeting to attempt the construction of a common system of nomenclature for the other classes of organic compounds.

He was awarded the Davy medal by the Royal Society in 1880; received the degree D.C.L. from Oxford University in 1894.

The following societies conferred their membership or honorary membership on Friedel: Foreign member of the English Chemical Society, 1876; Industrial Society of Mulhouse, 1879; Physical Society of Geneva, 1880; Royal Society of Turin, 1882; Academy dei Lincei, 1883; Academy of Munich, 1883; Royal Academy of Lisbon, 1890; Natural History Society of Maxon, Society Antonio Alzato Mendio, 1890; Roy Society of Brussels, 1892; Society of Physics and Chemistry of Bucharest, 1892; Literary and Philosophical

Society of Manchester, 1892; honorary member of the German Chemical Society, 1894; Royal Society of Sweden, 1894; corresponding member of the British Association for the Advancement of Science, 1895; Royal Society of St. Petersburg, 1895; Physical Society of Frankfort, 1898.

He was made Chevalier of the Legion of Honour in 1869, and Officer in 1886. He was Officer of Public Instruction, and was also Commander of the Orders of St. James of Portugal and of the Crown of Roumania.

Before taking up the record of Friedel's work in science, a further description may be given of the fortunate surroundings, which not only favoured the development of a judicious and amiable character, but also gave full play to his scientific ability. His tastes found immediate and hearty appreciation and support from his parents and relations, and sufficient pecuniary resources were always at his command to allow him to do his chosen work in the best way.

His love of science was hereditary. His father, Charles Friedel, although beginning his long commercial career in a banker's office at the age of thirteen, attended scientific lectures at Strasbourg whenever he had the opportunity, and, at the age of eighty-four, expressed his regret that necessity had prevented him from following a scientific career, and his satisfaction that the choice had been offered to his son.

The mother was a woman of strong character, and came of a professorial family. Her father was George Louis Duvernoy, a physician established at Mountbéliard, and later Dean of the Strasbourg Faculty of Science, and finally Professor at the Museum of Natural History at Paris.

The gathering of a small collection of minerals by the boy was encouraged, a laboratory was tolerated in his father's house, and later, when he was staying with his grandfather Duvernoy, he was aided in his choice of studies by the veteran in science, until failing health made the older man dependant upon the younger. A letter written in 1854 describes occupations which are not generally attributed to a student in the gay capital; thus the day was devoted to arduous studies to prepare for the baccalaureate examination, long evenings were spent in watching with or reading to the grandfather, and on Sundays some hours were given to visiting the poor.

Senarmont, with whom he began mineralogical work, took a strong and friendly interest in the young student, and Friedel's friendship with Wurtz was a very important factor in his career. Both Alsacians, united by tastes, opinions, and pursuits, the elder chemist opened the way for the younger in professional and editorial work Wurtz's high reputation, his activity in public affairs as well as in science, led to the creation of the chair of organic chemistry at the

Sorbonne, and after Wurtz's death in middle age, Friedel's studies and talents naturally marked him out as the successor. Wurtz's influence in Government circles also prevailed, after long-continued effort, in obtaining support for laboratory instruction, and, shortly before his death, the orders were given for the construction of a large modern laboratory at the Sorbonne, the plans of which were matured, and the construction superintended, by Friedel.

The two friends were very intimate, and were thoroughly in accord regarding all matters of public and scientific interest, but in later years Wurtz became much occupied with duties connected with his senatorship, whilst Friedel was never diverted from scientific pursuits. In consequence, the share of the latter in editing Wurtz's chemical dictionary became larger.

Until within a few years of his death, Friedel never had a well-equipped laboratory provided with labour-saving contrivances, nor was he disposed to have much work done by assistants, preferring to leave very ample opportunities to all those about him for doing original work and publishing it alone, whilst aiding them untiringly with his counsels. For these reasons, the volume of his contributions to chemical research is not very large, and many an idea passed into other hands for execution.

Most of the work in organic chemistry was done in a small room in the fine palace on the Luxembourg Gardens which is used for the School of Mines, whilst a dark, vaulted cellar served for the artificial production of minerals at high temperatures and pressures. Here Friedel and Edmond Sarasin heated "Jacob" to a very low red heat at whatever pressure boiling water gives at that temperature. The origin of the name is lost, but "Jacob" was the only designation of a very heavy steel tube lined with platinum, in which water and pure materials intended to make silicates were heated overnight, and the fate of "Jacob" was a matter of lively interest each morning in the laboratory. There was no serious explosion, but any attempt to economise in the weight of the thick interior platinum tube led to a disaster.

Friedel married Miss Emilie Koechlin of Mulhouse on December 29th, 1856. One son and four daughters were born of this marriage. The surrender of Paris in 1871 brought to him the sad news of the death of his charming and amiable wife, who had been obliged by failing health to pass the winter at Montreux and died on January 19th, 1871, while her husband was serving in the national guard during the siege. On April 7th, 1873, he married Miss Louise Combes, daughter of the director of the School of Mines, and a son was born of the second marriage. The character and education of his wife, who still survives, made her a most efficient aid and companion. During his last illness,

his wife and several of his children were with him at the house of his son-in-law, Professor Henri Bois at Montauban.

Friedel's life in Paris was wholly devoted to science, and was not unlike that of the professor in a university town. Weekly evening receptions kept him in touch with his scientific friends and scholars. In the discussions which took place on these occasions, his modesty led him instinctively to play the part of a listener until every one had expressed an opinion, and then all were glad to hear a new and fundamental treatment of the subject from Friedel's lips. It is a piece of good fortune for an honest man to have a face expressive of character, and his was eminently one which immediately convinced a new acquaintance that the man was incapable of guile, and thus inspired ready confidence and the ease of intercourse which goes with it.

He was a lover of music and of art, and his favourite recreation was sketching from nature. He took a strong and judicious interest in political affairs. Very happy in his family life, and in many intimate friendships, escaping unfriendly rivalries by his character and circumstances, he was permitted from the beginning to the end to carry on with a single mind the pursuits which he loved. The pursuit of science and his duties as a husband, father, friend, and citizen made up Friedel's existence. He was always disposed to work somewhat beyond his strength, and in 1885 a severe illness diminished considerably for the remaining years his capacity for experimental work, but not for editorial labours.

One of the elements contributing to a certain retirement from the disturbing interests of life in the French capital were the associations into which Friedel's Protestant faith (*Eglise réformée*) led him. Isolation is too strong a word to be applied to Protestant society at Paris, and yet in certain ways their habits of thought are different from those of their neighbours. Strong motives for these differences still survive among the Protestants of the older generation from the south of France, and the second wife of Friedel cannot forget having passed her childhood near Nismes in a house where the coffins of her relations occupied one of the drawing rooms because, as Protestants, they were refused Christian burial. No memories of persecutions haunt the immediate past of the Alsacian Protestants. Those who elected French nationality after the war, or who, like Friedel, were fortunate in having already chosen their residence in Paris, have had full recognition of their patriotism and of their value as citizens; nevertheless, a mental barrier is raised to some extent between Protestants and Catholics, and curious testimony of this attitude was lately offered when the latter joined with an army of Freethinkers and affected to confound the Protestants with the Jews. Not religious controversies, but different habits of thought, as marked as racial characteristics

make a distinct, although faint, line of separation between general Parisian society and that in which Friedel moved. For a man of his character, it must not be supposed, however, that any distinct obstacle prevented perfect freedom of intercourse with men of all shades of opinion.

After very deliberate reflection, the writer cannot forbear adding a piece of personal testimony to this sketch of a life's work. During thirty-eight years in which a close friendship made him a witness of conduct and actions, he cannot recall a single instance in which he would have wished his friend to have thought or acted otherwise than he did.

Chemical Researches.

Friedel at the age of twenty-five chose the ketones (acetones they were called at that time) for the subject of his first research, and he was fortunate enough to establish experimentally the properties of the first of the important series of secondary alcohols, besides preparing many new ketones and their derivatives (*Ann. Chim. Phys.*, 1869, [iv], 16, 310). While preparing new substances, he held the theoretical side of the subject distinctly in view, and did much to set it on a firm basis.

At this period, Gerhardt was the authority on organic chemistry. The type theory had been well developed, and owed much of its value to the discoveries of the compound ammonias and the bivalent alcohols by Wurtz. Kekulé, in the first volume of his organic chemistry, published in 1861, used the existing ideas of types and radicles in a much more rational way than his contemporaries, but there was some confusion in the use of what he called rational and reactional formulæ, and much remained to be done in presenting schemes of structure capable of explaining the relation between the constitution and properties of a substance. With greater or less distinctness, the chemists of the day recognised the possibility of explaining functions by formulæ, and Friedel was the first to so enlarge the data as to give what were accepted as convincing proofs of the dependence of the functions of the CO group in acetones upon the form of combination.

Kekulé devotes only seven pages in his first volume to the known ketones; he does not mention them under the section "Carbonyl compounds," and he uses five formulæ for acetone:

I.	II.	III.	IV.	V.
$\left.\begin{matrix}C_2H_3O\\CH_3\end{matrix}\right\}$	$''CO\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$	$C_3H''_6O$	$\left.\begin{matrix}C_3H_5O\\H\end{matrix}\right\}$	$\left.\begin{matrix}C_3H_5O\\H\end{matrix}\right\}$

The first two he calls rational formulæ, and probably considered II to be a developed form of I and V of IV. On page 617, he says that

the mesityl compounds point to V as the rational formula for acetone; the remaining reactions are explained by III.

It is unnecessary to give a catalogue of the new ketones obtained by Friedel, using known methods. In his first paper (*Compt. rend.*, 1857, **45**, 1013), he describes phenyl methyl ketone and methyl butyl ketone. He also studied the products of the action of phosphorus pentachloride on the ketones, obtaining a new propylene dichloride and monochlorinated propylene. The chief purpose of this work was to furnish further proofs of a similarity of function between aldehydes and ketones. This had already been indicated by certain reactions common to both series. Thus Limpricht had described the additive compounds with sodium hydrogen sulphite, and Städeler those with hydrocyanic acid. Cahours had shown that an aldehyde treated with phosphorus pentachloride does not break up like an alcohol or an ether, but that two atoms of chlorine are substituted for oxygen. Friedel completed the demonstration by showing that acetone behaved in the same way.

Friedel, in a second paper (*Compt. rend.*, 1862, **55**, 53), described the behaviour of aldehydes and ketones on reduction with sodium amalgam (zinc and an acid cannot be employed because the production of hydrogen is arrested by aldehydes). Wurtz had used the sodium reduction for ethylene oxide, but was prevented from applying it to aldehydes because of the resinifying action of caustic soda on common aldehyde. Friedel succeeded in reducing benzaldehyde and valeraldehyde to the corresponding alcohols, and acetone to a propylic alcohol, which was not identical with the primary one (b. p. 97·3°) discovered by Chancel in 1853 among fermentation products. He believed it to be identical with a propylic alcohol prepared by Berthelot in 1855 by the action of sulphuric acid on propylene.

No experiments had been made to prove that Chancel's alcohol gave propionic acid and Berthelot's alcohol acetone on oxidation, and Friedel considered it superfluous to ascertain whether a substance derived from acetone by reduction would give acetone on oxidation. Kolbe took advantage of this omission to bring forward his theoretical views, predicting this nearly evident fact, and at the same time giving a clear exposition of the difference between a primary and a secondary alcohol. The capital point was the discovery of the relation of a secondary alcohol to its oxidation product, and it may be considered that Friedel's reduction of acetone accomplished this task.

Berthelot (*Ann. Chim. Phys.*, 1855, [iii], **43**, 399) afterwards tested the alcohol derived from propylene, and found that it also gave acetone on oxidation.

It should be stated that Kolbe recognised more clearly than the other chemists of that time the significance and the importance of the

existence of two kinds of propylic alcohol, one of them offering the first example of a secondary alcohol.

Friedel also observed the formation of pinacone, and pointed out its true constitution. It had been discovered by Fittig, and supposed to be a hydrate of $C_6H_{12}O$. Later, in 1873, Friedel and Silva (*Bull. Soc. Chim.*, [ii], **19**, 289) described a process for the convenient preparation of large quantities of pinacone.

The True Formula of Lactic Acid.—Wurtz and Friedel (*Ann. Chim. Phys.*, 1861, [iii], **63**, 101) showed the difference between the alcoholic and the acid functions of the two hydroxyl radicles in lactic acid, and the corresponding properties of the two esters. They explained that lactic acid is intermediate between propyl glycol and malonic acid, as glycollic acid is intermediate between glycol and oxalic acid. The alcoholic hydroxyl they call basic.

Friedel and Machuca (*Compt. rend.*, 1861, **52**, 1087) described the synthesis of lactic acid from bromopropionic acid, glyceric acid from dibromopropionic acid, hydroxybutyric acid from bromobutyric acid, and butalanine by the action of ammonia on bromobutyric acid.

The Theory of Double Decompositions.—Friedel and Crafts (*Compt. rend.*, 1863, **57**, 877, 986) showed that when the ester of an alcohol is heated with another alcohol, one radicle partially displaces the other as one metal displaces another in salts. Mixed esters of polybasic acids are formed by a similar process. Alkyl iodides heated with esters give rise to similar displacements, but here a little hydrogen iodide is set free, and serves to esterify a large quantity of alcohol.

Friedel subsequently made a contribution to the theory of esterification by means of halogen acids by showing that, in presence of phosphoric oxide, hydrogen chloride converts a considerable proportion of benzoic acid into benzoyl chloride, and supposes that a similar transformation contributes to esterification (*Compt. rend.*, 1869, **68**, 1547).

The experimental difficulties of these early problems were not great, and chemists were rewarded for their labours by the rapid appearance of new substances; the next research led on to more difficult ground.

Silicon Compounds.—Friedel's interest in mineralogy led him to take up the important question of the atomic value of silicon. The school of Wurtz had completely accepted the authority of Avogadro's law under which $SiCl_4$ represents the molecule of the best known volatile compound of silicon; but Buff and Wöhler discovered in 1857 a compound, $Si_2Cl_3 2HCl$ (Si = 21), whose formula is incompatible with the quadrivalence of silicon. They described the new substance as a liquid boiling at 42°, obtained by the action of hydrogen chloride on silicon. This support for the old tervalent formula was welcomed by all those who had been accustomed to the calculations of mineral analyses established by Berzelius. The new discovery, however, did

not convince Friedel, who considered that, beside the vapour density of silicon tetrachloride, the work of Marignac and the whole assemblage of facts pointed to the tetratomicity of silicon, and sought a confirmation of his views in the organic compounds of the element.

Friedel and Crafts (*Compt. rend.*, 1863, **56**, 324; **57**, 319) took up the work of Ebelmen (*Annalen*, 1844, **52**, 324; 1846, **57**, 319), expecting to find that the normal ester $Si(OEt)_4$ would form a series of condensed esters of which the simplest, upon a quadrivalent scheme, must be $Si(OEt)_3 \cdot O \cdot Si(OEt)_3$. It was proved that this compound, and others more complicated, for example, $Si(OEt)_3 \cdot O \cdot Si(OEt)_2 \cdot O \cdot Si(OEt)_3$, were produced by the action of a trace of water on the normal ester. The first of the series can be easily purified by fractional distillation; but the boiling points of the other members, even in a vacuum, are so high that a separation becomes impossible, since they boil at temperatures at which glass softens, without giving off much gas, but undergoing polymeric transformations. The quadrivalent character of silicon was also shown by allowing anhydrous alcohol to act on an excess of silicon tetrachloride, when a series of well defined chlorohydrins was obtained with the formulæ $SiCl(OEt)_3$, $SiCl_2(OEt)_2$, $SiCl_3OEt$. The composition and vapour densities of these substances agree only with the atomic weight 28 for silicon.

The polysilicic esters recall the series of polyglycols and the analogy between the quadrivalent elements, silicon and carbon, was so marked in all these organic compounds, that it seemed desirable to attempt to replace carbon by silicon in a hydrocarbon and to endeavour to make silicononane SiC_8H_{20}. It was thought that this domain might belong to Professor Frankland, but after consulting him Friedel and Crafts were courteously informed that the research was open to them, Professor Frankland stating that the few attempts which he had made to obtain a reaction between silicon chloride and zinc ethide had not been successful. A rather high temperature is required and some gas is produced, but large quantities of a pure substance, $Si(Et)_4$, distilling at 153° were prepared. Unlike most organo-metallic compounds, this substance is very stable towards all reagents, and has completely the aspect of a hydrocarbon except that when it burns, it forms a smoke of silica. In it, chlorine can be substituted for hydrogen and then hydroxyl for chlorine, giving siliconony lic alcohol, $SiC_8H_{19} \cdot OH$. In the same way that petroleum hydrocarbons are accompanied by small quantities of oxidation products, mostly ketones and alcohols, so also silicon tetrethide, both during its formation and afterward by contact with air, is liable to an oxidation more rapid than petroleum, but still very slow. On account of oxidation, some difficulty was experienced in obtaining the silico-hydrocarbon pure until the oxygenated products were separated

by solution in concentrated sulphuric acid, which does not attack the hydrocarbon. Thus an unmistakable analogy is established between the general character of carbon and silicon compounds, and Friedel afterwards made use of this resemblance in building up rational formulæ for mineral silicates.

Silicic esters of other alcohols were prepared and also silicon tetramethide, but with much more difficulty than the ethide.

It may be noticed that when the esters are slowly decomposed by penetration of moisture during many years, an opaline silica, hard enough to scratch glass, is obtained.

Friedel and Ladenburg (*Bull. Soc. Chim.*, 1867, [ii], **7**, 322) took up the study of Buff and Wöhler's silicon hydrochloride, $Si_2Cl_3,2HCl$ (Si = 21), and showed that it could be separated by fractional distillation into silicochloroform, $SiHCl_3$, boiling at 36°, and silicon tetrachloride, $SiCl_4$, boiling at 55—60°. By action of alcohol, the former gives $SiH(OEt)_3$, and with water an oxide, $Si_2H_2O_3$, which corresponds with formic anhydride containing silicon instead of carbon.

An impure silicon hydride was described by Buff and Wöhler; the pure compound was prepared by the action of sodium upon the ether $SiH(OEt)_3$.

Friedel and Ladenburg (*Annalen*, 1868, **145**, 174) found that a sulphide to which Pierre gave the formula $SiCl_2S$ (Si = 21) really contained hydrogen and was a silico-trichloromercaptan, $SiCl_3SH$. The SH radicle can be replaced by bromine to obtain $SiCl_3Br$.

Friedel and Ladenburg (*Compt. rend.*, 1868, **66**, 530) obtained $SiCl_3{\cdot}O{\cdot}SiCl_3$ by passing silicon tetrachloride through a red hot porcelain tube, the oxygen being taken from the porcelain. This oxychloride gives with alcohol the same ester, $Si(OEt)_3{\cdot}O{\cdot}Si(OEt)_3$, as that obtained by the action of water on the ortho-ester $Si(OEt)_4$. With zinc ethide, it gives $SiEt_3{\cdot}O{\cdot}SiEt_3$ and this oxygenated compound seems also to be formed in the preparation of silicon ethide.

Silicon tetriodide, SiI_4, and silico-iodoform, $SiHI_3$, were prepared by the action of iodine and hydrogen iodide on heated silicon, and Buff and Wöhler's formula, $Si_2I_3,2HI$, for the product of the reaction, was shown to be erroneous (Friedel, *Bull. Soc. Chim.*, 1868, [ii], **9**, 1). The compound, $SiBr_3I$, boiling at 200° was obtained by the action of bromine on silicon tetriodide, SiI_4.

Silicon triiodide, Si_2I_6, was obtained by heating the tetriodide, SiI_4, with finely divided silver at 300° (Friedel and Ladenburg, *Compt. rend.*, 1869, **68**, 920); a non-volatile substance, SiI_2, was also obtained which yields hydrogen on treatment with potassium hydroxide. The hexaiodide reacts with water to give the compound $Si_2O_2(OH)_2$, which may be regarded as oxalic acid, in which carbon is replaced by silicon.

From the triiodide, the trichloride, Si_2Cl_6, boiling at 146°, was ob-

tained by treatment with mercuric chloride (Friedel, *Ber.*, 1869, **2**, 747), and the ethide, $Si_2(C_2H_5)_6$, by the action of zinc ethide.

Silicopropionic acid, $C_2H_5Si{\cdot}O{\cdot}OH$, was prepared by the action of zinc ethide on the chlorohydrin, $SiCl(OC_2H_5)_3$, and subsequent saponification of the product.

This brilliant investigation by Friedel and Ladenburg, in which frequently great experimental difficulties were overcome, established with unhoped-for completeness the strong analogy between silicon and carbon compounds.

Titanium Compounds.—Friedel and Guérin (*Compt. rend.*, 1875, **81**, 889), by the action of silver, reduced titanium tetrachloride, $TiCl_4$, to the trichloride Ti_2Cl_6, but found that when an attempt is made to purify the latter by distillation, it breaks up into the dichloride, Ti_2Cl_4, and tetrachloride, $TiCl_4$. By interaction with bromine, the dichloride gives the compound $TiCl_2Br_2$. Bromine converts the trichloride, Ti_2Cl_6, into the compound $TiCl_3Br$; the oxychloride, $TiOCl_2$, was also prepared.

In the description of Friedel's mineralogical work will be found an account of titanic oxides derived from these chlorides.

Friedel and Guérin (*Ann. Chim. Phys.*, 1876, [v], **8**, 24) also studied the compounds of titanium with nitrogen, and isolated the nitrides, Ti_2N_2 and Ti_3N_4.

Mixed Halogen Compounds of Hydrocarbons.—Friedel and Silva (*Jahresb.*, 1870, 419; *Compt. rend.*, 1871, **73**, 955; *Bull. Soc. Chim.*, 1872, [ii], **17**, 537) found that only one-half the bromine in bromopropylene is replaced by chlorine when treated with mercuric chloride; with ethylene chlorine, the action is complete at 180°, and all the chlorine is replaced. They obtained 1 : 2-dichloropropylene, 1 : 3-dichloropropylene, and 2 : 3-dichloropropylene by new modes of synthesis. The physical constants and chemical reactions of these bodies were determined, and so far as the methods of the day permitted, their rational formulæ were fixed.

The action of iodine monochloride on chloroform was found to give rise to carbon tetrachloride, CCl_4 (Friedel and Silva, *Bull. Soc. Chim.*, 1872, [ii], **17**, 537); with ethylene or propylene, iodine monochloride formed dichlorides with separation of iodine.

Synthesis of Glycerol.—Friedel and Silva (*Compt. rend.*, 1871, **73**, 1379; 1872, **74**, 805) undertook the synthesis of glycerol from the elementary components. At this time, although it was recognised that the rapidly increasing number of such syntheses held out a prospect for making all natural products artificially, yet few means were at hand for supplanting the work of nature, and the synthesis of glycerol had not been accomplished. So soon as the true formula was known, $CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, the only

difficulty lay in attaching a halogen atom to each of the three carbon atoms. At first, allyl iodide was used for the preparation of trichlorohydrin, but afterwards, in answer to an objection from Berthelot that allyl derivatives came from glycerol, propylene was prepared from acetone, and by treating this with chlorine and with iodine monochloride, trichlorohydrin was obtained, which was easily transformed into glycerol.

Dimethyldiethylmethane was one of the most important substances prepared during an extended study of the products of the action of the halogens on the simpler hydrocarbons. It was the first example of the type CR_4, and was prepared by the action of zinc ethide on dimethylmethylene dichloride, $(CH_3)_2CCl_2$ (Friedel and Ladenburg, *Compt. rend.*, 1866, **63**, 1083).

A new mode of preparing allylene was discovered in the action of caustic potash on dimethylethylene chloride, $CCl_2(CH_3)_2$ (Friedel, *Compt. rend.*, 1864, **59**, 294), and of phenylacetylene in the action of caustic potash on the compound $C_6H_5{\cdot}CCl_2{\cdot}CH_3$ (Friedel, *Compt. rend.*, 1868, **67**, 1192).

Dimethyl Ether Hydrochloride.—At a time when it was imperfectly recognised that the variations from the law of Avogadro were due to dissociation, Friedel discovered a compound whose dissociation was complete at a very low temperature: namely, the combination of methyl ether and hydrogen chloride, $6C_2H_6O,5HCl$, a liquid boiling at $-2°$. Friedel studied the dissociation tension of this substance at various temperatures, and concluded it was a true chemical compound, although highly dissociated in the gaseous state (*Compt. rend.*, 1875, **81**, 152, 236).

*The Aluminium Chloride Reaction.**—The experiments which demonstrated the wide scope of the reaction were so easy of execution that those described in the first three papers were carried out in the course of five or six weeks. The discovery sprang from an accidental observation of the action of metallic aluminium on chloride of amyl. It was soon seen that the metallic halogen salt and not the metal was the active body, and a similar fact was found to give the true explan-

* The first publications were made in 1877 (*Compt. rend.*, **84**, 1392, 1450; **85**, 74). A complete account of work done up to 1887 is given in the *Annales de Chimie et Physique*, 1884, [vi], **1**, 449; 1887, **10**, 411; **11**, 263; and 1888, **14**, 433). A good presentation of the literature of the aluminium chloride reaction is to be found in Elbs' *Synthetische Darstellungs Methoden* (vol. ii, pp. 140—171). He says that the Friedel-Crafts reaction is among all synthetical methods the one most commonly used, and cites a nearly complete list of its employment by its discoverers and its extension by other chemists. A curiosity in chemical literature is the book of 864 pages by Seelig upon organic reactions which makes 23 citations of 20 authors concerning the aluminium chloride reaction without mention among them of the name of Friedel.

ation of the excellent synthetical method discovered by Zincke (*Ber.*, 1873, 6, 137), in which zinc dust and benzyl chloride were used to obtain diphenylmethane. So sensitive is the reaction in some cases that benzyl chloride is decomposed by long distillation in a copper vessel if brass solder has been used, zinc chloride taken from the solder being the condensing agent.

The results obtained in the very beginning seemed to show that any number of halogen atoms in a paraffin could be replaced by phenyl; that the six hydrogen atoms in the benzene ring could each, with equal ease, be replaced successively by alkyls; and that a halogen in an aromatic side chain acted with even more readiness on the benzene ring. Halogens substituted in the aromatic ring were inactive in presence of aluminium chloride even at high temperatures. Some few exceptions were found later to these generalisations. All these reactions between chlorinated compounds and aromatic hydrocarbons took place at the ordinary temperature, or with slight warming in presence of aluminium chloride, bromide, or iodide. Zinc or ferric chloride had a similar effect, but in a less degree. Chlorides of magnesium, cobalt, copper, mercury, and antimony are without effect.

The chlorides of mono- or di-basic acids react with benzene and its homologues, giving ketones. The presence of alcohol or acids, that is, of hydroxy-compounds, prevents the aluminium chloride reaction, and it also could not at first be carried out with ethers. New compounds were obtained, like phthaloketone and pentamethylbenzene, and the way was immediately opened for preparing with great ease numerous homologues of benzene and new ketones. The preparation of such hydrocarbons as durene and hexamethylbenzene was made easy, and consequently mellitic acid could readily be obtained by a process of oxidation. Also, triphenylmethane and its homologues were prepared on a large scale, and these seemed to offer a new method of making aniline dye stuffs commercially. Unfortunately, the discoverers had at that time only a very small laboratory, with no place for students, and not even provided with the convenience of running water, whilst circumstances separated them for a time and retarded the progress of the work in clearly indicated directions.

The first publication in 1877, beside containing a record of the facts above stated, offered a theory of the reaction based upon analogies with the properties of organo-metallic bodies. It was supposed that all the observed effects might be explained by the existence, even in small proportion, of an organo-metallic chloride, $C_6H_5 \cdot Al_2Cl_5$, which, being constantly decomposed according to the equation $C_6H_5Al_2Cl_5 + RCl = C_6H_5R + Al_2Cl_6$, and constantly renewed, would explain the contact action of aluminium chloride. This theory was kept in view

throughout subsequent work, and was strengthened by many new facts, and particularly by those relating to the readiness with which oxygen, sulphur, carbon and sulphur dioxides, and cyanogen are absorbed by the benzene compound with aluminium chloride, giving respectively phenol, phenylmercaptan and phenyl sulphides, benzoic acid, phenylsulphonic acid, and benzonitrile. The small quantity of each of these products obtained may be ascribed to the insolubility of the gases in benzene.

The action of the compound $C_6H_5AlCl_5$ should be analogous to that of aluminium triphenyl, $(C_6H_5)_3Al$. The latter was prepared by the action of aluminium on mercury diphenyl, and gives, with benzyl chloride, diphenylmethane; with oxygen, phenol; and with sulphur, phenylmercaptan, but has no action on halogens substituted in the benzene ring. Hence a well-known organo-metallic compound gives the same reactions as aluminium chloride and benzene.

Zinc ethide is known to break up by heating into ethylene and ethane. Here, again, the analogy holds good, for hydrocarbons heated with aluminium chloride break up into simpler saturated compounds which are easily isolated, and into complex non-saturated ones. The latter are probably derived from simple unsaturated substances, C_nH_{2n} or C_nH_{2n-2}, &c., which undergo condensation in presence of aluminium chloride, a reaction which can be observed in the simplest stage between benzene and ethylene, $C_6H_6 + C_2H_4 = C_6H_5 \cdot C_2H_5$. The condensation proceeds much further when halogen derivatives of the paraffins are treated with aluminium chloride, undistillable products very poor in hydrogen being formed, together with volatile paraffins.

The last investigation of Friedel in this field concerned the action of aluminium chloride on one of the simplest of the paraffins, and, in conjunction with Gorgeu (*Compt. rend.*, 1898, 127, 590), it was found that normal hexane treated with aluminium chloride at 35° gives pentane and butane together with condensed products.

The aromatic hydrocarbons are usually more stable, but they are all decomposed by heating with aluminium chloride at high temperatures. Naphthalene is very easily attacked, giving benzene and an excellent yield of hydrides of naphthalene. Triphenylmethane is also easily decomposed, giving diphenylmethane, toluene, and benzene. Benzene gives diphenyl and other products.

The alkyl groups in aromatic compounds are subject to migrations giving rise to higher and lower homologues. These changes and isomeric transformations of chloro-paraffins were found to limit the possibilities of the reaction.

The action of aluminium chloride on substances associated with petroleum, and the elimination of sulphur from them, was studied.

In consequence of the claims of various authors to have discovered the destructive action of aluminium chloride, a restatement was made of the original facts with some additions (Friedel and Crafts, Trans., 1882, **41**, 115; *Compt. rend.*, 1885, **100**, 692).

Exceptions to the general rules were discovered later. In some cases, ortho-dihalogen substitution products in the benzene ring are attacked. In $CH_2Cl{\cdot}COCl$, only the chlorine in the carbonyl group is active, and in the case of carbon tetrachloride only three atoms of chlorine are replaced by phenyl, and diphenyl is formed as a bye-product, as was shown by Fischer. The mistake in the first paper, which announced the formation of tetraphenylmethane, was due to an error in Watt's Dictionary, 2nd Suppl., p. 948, which gives 335° for the boiling point of triphenylmethane. The product isolated boiled 24° higher, namely, at 359°, and was therefore assumed to be a tetraphenyl compound, the percentage composition of the two compounds being not far different. Subsequent determinations made by Crafts with a hydrogen thermometer showed 359° to be the boiling point of pure triphenylmethane.

The synthesis of triphenylmethyl was studied anew in 1882 (*Bull. Soc. Chim.*, [ii], **37**, 6), and the conditions for obtaining a good yield were described. The proportion of diphenylmethane produced as bye-product is only about one-fourth that of the triphenylmethane. Triphenylcarbinol was obtained from the product of the interaction of carbon tetrachloride and benzene by treatment with water.

These are the principal facts which characterise the reaction, and which have a bearing upon its theoretical explanation; it is only necessary to cite a few examples of its use in preparing pure products.

A class of ortho-ketonic acids is easily obtained by means of the anhydrides, such as phthalic anhydride, $C_6H_4\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle O + C_6H_6 = C_6H_4\langle\begin{smallmatrix}CO{\cdot}OH\\CO{\cdot}C_6H_5\end{smallmatrix}$.

Phthalic chloride, $C_6H_4\langle\begin{smallmatrix}CCl_2\\CO\end{smallmatrix}\rangle O$, treated with aluminium chloride and benzene, gives phthaloketone, $C_6H_4\langle\begin{smallmatrix}C(C_6H_5)_2\\CO\end{smallmatrix}\rangle O$. It was hoped to effect the synthesis of anthraquinone by this reaction, but the yield is very poor. It suffices, however, to indicate the existence of a symmetrical phthalic chloride which gives the reaction $C_6H_4\langle\begin{smallmatrix}COCl\\COCl\end{smallmatrix} + C_6H_6 = C_6H_4\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle C_6H_4 + 2HCl$.

Anthracene and its homologues can be obtained by a reaction which takes place according to the equation $3CH_2Cl_2 + 3C_6H_6 = C_2H_2(C_6H_5)_2 + C_6H_5{\cdot}CH_3$. The principal product, however, is diphenylmethane.

When toluene is substituted for benzene, dimethylanthracene is formed.

The fundamental synthesis of a ketone by the action of carbonyl chloride on benzene in presence of aluminium chloride takes place with such regularity that when pure crystallised benzene is used, the crude product boils within a limit of 0·2°, and forms the best substance for standardising thermometers near 306°.

Vapour Density Determinations.—The molecular weight of aluminium chloride was found by Nilson and Pettersson to approach that required by the formula $AlCl_3$, and consequently to accord with the tervalent place usually assigned to aluminium in the periodic arrangement of the elements (*Zeit. physikal. Chem.*, 1887, 1, 459).

Friedel and Crafts (*Compt. rend.*, 1888, **106**, 1764; **107**, 306) drew attention to the fact that the experiments of Nilson and Pettersson began at 440°, and that the method of Victor Meyer, which was used, is unsuitable for determinations near the boiling point of the substance. The physical properties of aluminium chloride were studied, and a careful series of determinations of the boiling point of aluminium chloride between the pressures of 252 and 2277 mm. of mercury were made. The chloride was liquefied under pressure, and crystallised in beautiful, white, transparent crystals melting at 186·5°, or a little above the boiling point under atmospheric pressure, namely, 183°.

Vapour density determinations by Dumas' method, modified to obtain different tensions, were made between 218° and 432°, and the vapour density was found to correspond with that required by the molecular formula Al_2Cl_6.

Under similar conditions, vapour densities corresponding to the formulæ Fe_2Cl_6 and Ga_2Cl_6, were found for ferric and gallium chlorides.

Camphoric Acid.—Friedel (*Compt. rend.*, 1891, **113**, 825; *Bull. Soc. Chim.*, 1893, [iii], **9**, 27) gave various experimental proofs that camphoric and isocamphoric acids contain, like lactic acid, two hydroxyl groups with different functions, one of them nearly alcoholic. Four esters were described, and a hypothesis regarding the constitution of camphor, with particular reference to the stereochemical formulæ of right and left rotating camphoric and isocamphoric acids, was illustrated with diagrams.

A method of analysis of isomeric xylenes and ethylbenzene was founded upon the fact that the xylenes, when treated with a large excess of bromine and a little iodine, form tetrabromo-substitution products nearly insoluble in light petroleum, and by that means separable from the dibromethylbenzene formed under the same conditions. The tetrabromoxylenes can be oxidised quantitatively to the corresponding tetrabromophthalic acids by treatment at 160—170° with bromine

and water, and the acids separated by precipitation (Friedel and Crafts, *Compt. rend.*, 1885, **101**, 1218).

Armstrong and Miller published a description of the now well known and convenient mode of decomposition of sulphonic acids in sulphuric acid solution by means of steam, and the priority belongs to them; but before the method was made public, Friedel and Crafts had begun its study from a somewhat different point of view, and endeavoured to utilise the different temperatures at which the reaction takes place, in order to separate hydrocarbons, and in particular the hydrides of naphthalene from naphthalene (*Bull. Soc. Chim.*, 1884, [ii], **42**, 66). Phosphoric acid was afterwards used as a solvent instead of sulphuric acid, in order to avoid the destructive and oxidising action of the latter (*Compt. rend.*, 1889, **109**, 95).

Thiophosphates in well crystallised forms were obtained by heating the calculated quantities of phosphorus and sulphur with iron, aluminium, copper, lead, and silver to dull redness in sealed tubes. The general formula is $M_4P_2S_6$. Thioselenium salts were also obtained (Friedel, *Bull. Soc. Chim.*, 1894, [iii], **11**, 1057; Friedel and Chabrié, *Bull. Soc. Chim.*, 1895, [iii], **13**, 163).

An examination of fat from an Egyptian tomb showed that the glycerol had completely disappeared, apparently through oxidation. Palmitic and stearic acids were found unchanged, and azelaic and pimelic acid had been produced by oxidation (*Compt. rend.*, 1897, **124**, 648).

Mineralogical Researches.

Friedel's work in mineralogy was of capital importance and marks a transition period in the history of that branch of science. After mineralogical cabinets had been filled with natural specimens, their sources duly noted, and when each species had been analysed, measured, and arranged, the old fashioned mineralogist seemed to have accomplished his task. To a collector of an antiquarian turn of mind, only those specimens which came from veins, druses, or rocky beds were of prime interest, whilst chemical or metallurgical products of similar composition, even when well crystallised, were set apart as new comers and not considered of equal rank with those whose landed title was well established. The geologist tried to describe the rocks in terms of mineral species, as chemical compounds are identified by the proportions of their elements; but only rarely were the conditions of formation of a species known or used to give testimony concerning the modes of formation of rocky strata. It was not duly appreciated that most crystalline rocks are a mixture of crystals with mother liquor, that purer specimens can be obtained by laboratory processes,

and that the essential constituents can be best determined by synthesis with pure materials.

Then came a period of synthetical mineralogy in which Friedel played an important part. It is evident that ideas regarding the igneous origin of an eruptive rock were confirmed if it contained the same crystalline species that could be observed in the slag of an iron furnace, and that the reproduction of minerals found in veins by sublimation or by crystallisation from water gave some evidence concerning natural processes. Moreover, some ideas concerning the effect of each of the different items contributing to the formation of a crystal can be gathered by the artificial production of the same crystal, under laboratory conditions of pressure, temperature, and presence or absence of water, each element in the experiment being subject to variation at will.

Friedel's equal skill as chemist and mineralogist enabled him to attack these problems to good purpose, and he pursued the subject with unswerving patience during his whole life, seeking to grow in a few days crystals which nature had passed ages in perfecting. Mineralogical problems were never excluded from his thoughts even at times when work in organic chemistry was progressing most successfully, and the delicate operations of these researches were performed by his own hands. New views of chemical composition, as, for instance, the hypothesis of the benzene ring, were immediately brought to bear on the formulæ of minerals, and the similarity of structure between the silicon and the carbon compounds with organic radicles, shown by his researches upon the silicon ethides, suggested new formulæ for silicates.

The details of his researches will show that many branches of experimental science were brought to bear upon his mineralogical work, and that from a very elevated standpoint he kept in view the paths by which mineralogy leads to geology, chemistry, and through delicate experiments in optical and pyro-electric phenomena, to the fundamental problems of molecular physics. His last illness cut short a research intended to offer final proofs of the necessary relation between rotatory power and the asymmetrical structure of carbon compounds.

Consciously or unconsciously he followed the lead of Pasteur in grouping his theories of the natural phenomena which came before him around a distinct conception of molecular arrangement from the point of view of a crystallographer.

The transference of his professorship from mineralogy to organic chemistry interrupted his work upon a mineralogical treatise of which the first part was published in 1893. This work was of elementary character and was particularly intended for the use of chemists. It

contains an exposition of geometrical crystallography, an original view of the principle of a chemical classification of minerals together with a discussion of the classifications of other authors, and an account of isomorphism and polymorphism. A second volume was to have followed containing descriptions of mineral species.

Friedel's papers were published in the *Comptes rendus*, the *Annales de Chimie et de Physique*, and *Bulletin de la Société Chimique* until, in 1878, he took part in founding the *Bulletin de la Société de Mineralogie*, and there published all his later work. He was most assiduous in attendance upon the meetings of the French Mineralogical Society and took an active part in its councils.

He published a lecture (*Revue Scientifique*, November 23rd, 1878) upon the work of his predecessor at the Sorbonne, Delafosse. Another lecture (*Revue Scientifique*, September 11th, 1880) gives a review of the methods previously employed for the artificial preparation of minerals. An address (*Bull. Soc. Miner.*, 1881, 4, 187), before the Mineralogical Society after the death of Henri St. Claire Deville, gives an account of the brilliant work of that chemist in the same field.

Crystallography.—At the time when Friedel began his mineralogical work, the pyro-electric phenomena in crystals did not appear to be always in accord with the ideas of symmetry and homogeneity of crystalline form developed by geometrical and optical studies. He undertook to show that the apparent anomalies were due to imperfect experiments, or to false interpretations, and with true scientific instinct commenced his review of the subject by the invention of improved methods of investigation. Of the two theses offered by him for the doctor's degree, one was upon pyro-electric phenomena in crystals. He verified Marbach's discovery of two varieties of pyrites of opposite thermo-electric signs ; the two often united in the same crystal. It was supposed that external hemihedral forms were an essential characteristic pointing to the pyro-electric phenomena. Such forms would be non-superposable, but Friedel showed that they do not occur in parahemihedral crystals, which, like pyrites, give thermo-electric currents, although mathematically it is possible to conceive of their existence. In natural specimens, holoaxial hemihedral crystals alone show these non-superposable forms. He concluded that some structure which does not give an external sign was responsible for the electric phenomena of opposite signs, and he attributed them in parahemihedral crystals to a molecular arrangement along axes symmetrical about a centre, like the tertiary axes of pyrites, but so placed that their extremities cannot be superposed.

In crystals which conduct electricity like pyrites, these axes should mark the directions in which pyro-electric phenomena would manifest themselves. He investigated the subject experimentally, and succeeded in demonstrating these properties with certainty and regularity, but

only after having made thin, parallel-faced sections of the crystals. With entire crystals, irregular results are obtained which are confusing and have led different experimenters to erroneous conclusions. Friedel was the first to recognise that the strong currents set up when a crystal of pyrites is cooling are due to irregular rates of cooling in the mass of the crystal, and his first care was to eliminate such phenomena by making thin sections. He then succeeded in making a model with a thermo-electric couple of bismuth and antimony which imitated the phenomena occurring when crystals of pyrites are heated, and thus confirmed his theory that the crystals contain at the same time two kinds of molecular arrangement with non-superposable axes giving rise to thermo-electric currents of opposite signs.

He found that parahemihedral crystals which do not conduct an electric current, as apatite, for instance, show no pyro-electric phenomena, and concluded that in general the pyro-electric phenomena are not due to hemihedrism, when it can be referred to a centre, and that the property does not exist in pyrites in consequence of the parahemihedrism, but is induced only by the existence of the above-mentioned molecular arrangement about non-superposable axes of which no indication is given by external form.

He then examined the rare antihemihedral crystals which are good conductors, panabase and chalcopyrites, and discovered a regular flow of a pyro-electric current, as in tourmaline.

The interesting fact was shown that currents always flow in the same direction as those which would be produced by thermo-electricity in a system of metallic tetrahedrons of the same thermo-electric sign, and arranged in the same position as the crystal, and thus the hypothesis is suggested that pyro-electric phenomena in crystals may be due to the currents set up by tetrahedral elements. This first research of the young mineralogist was distinguished by a clear conception of a hypothesis accounting for certain phenomena and excluding others. It passed through the test of controversy, for in 1871 G. Rose published statements concerning pyrites and cobaltine, and asserted that external forms distinguished the two pyro-electric varieties. Friedel (*Compt. rend.*, 1874, 78, 508) pointed out errors in these observations, and maintained his previous conclusions by new experiments. A better method of heating crystals (*Bull. Soc. Miner.*, 1879, 2, 31) was described, in which a hot metallic ball was applied to a cold surface. When this new device for heating was applied to thin sections of crystals, pyro-electric currents were shown in topaz normal to the plane of cleavage, the experiment contradicting statements by Ries and Rose, and pyro-electric currents parallel to the tertiary axes were found in blende.

Hankel had found pyro-electric phenomena in quartz: an observa-

tion which seemed to be at variance with the symmetry of this holoaxial crystal. Friedel showed that the pyro-electric direction corresponded only with binary axes, the edges of the prism being alternately of opposite sign. The fact, then, is in accord with the theory of symmetry; for there is no pyro-electricity displayed in the direction of the tertiary axis of which the two extremities are superposable, whilst it is shown where it would be expected in the direction of the binary axes, whose extremities are not superposable or symmetrical.

Subsequent investigations were made in conjunction with P. and T. Curie and with A. de Grammont, and these often took the form of a discussion with German crystallographers, because observations which appeared to contradict Friedel's views were again made by Hankel, and by Erman, Ries, and Rose.

The question required delicate handling, and the work of Friedel and his associates consisted in disengaging the phenomena which were purely pyro-electrical from others due to irregular internal tensions discovered by P. and T. Curie, and named by them piezo-electric; in other words, strains set up when a whole crystal cools irregularly are capable of producing electric currents.

In a paper published with T. Curie (*Bull. Soc. Miner.*, 1883, **6**, 191), Friedel showed that, when all disturbing influences are eliminated, no pyro-electric currents can be obtained from crystals of the tertiary system, or with hexagonal crystals, like quartz, having three axes of hemimorphism in the same plane, or even in antihemidral crystals of the cubic system, in which the four axes of hemimorphism mutually compensate. Corroborative experiments were made with blende and with sodium chlorate. With reference to this theory, boracite presents a curious example in the two forms which it assumes according to the temperature. Above 265°, it is cubic and isotropic, and is not pyro-electric; at 265°, it becomes suddenly orthorhombic, and on cooling below this temperature pyro-electricity is manifested.

Later (*Bull. Soc. Miner.*, **8**, 1885, 16), Friedel and T. Curie showed that a crystal of topaz, instead of being simply orthorhombic, as was held by Ries and Rose, and by other authorities, is composed of four clinorhombic individual crystals grouped about a central orthorhombic crystal. These five elements can be isolated by cutting, and a pyro-electric axis displayed parallel to the base, to which the central poles of Ries and Rose can be referred. He thus proved that the optical properties of topaz, pointing to an antihemihedral clinorhombic system grouped upon a rhombic centre, are in complete accord with the pyro-electric phenomena, namely, the central poles described above and a pyro-electric axis parallel with the axis of the prism. The twin formation of complementary crystals explains the accidental

occurrence of crystals whose two extremities have the same electric polarity.

Friedel and A. de Grammont (*Bull. Soc. Miner.*, 1895, **18**, 75) studied the pyro-electric properties of scolecite, and found that a similar analysis could be made of the pyro-electric axes. They discovered in this mineral a peculiar arrangement of twin crystals, in which the two extremities show at their junction the same polarity, and consequently the macle formation cannot be explained by a rotation around an axis perpendicular to the plane of junction. This curious case of want of symmetry about the plane of junction has proved interesting with reference to a theory put forward later by Mallard.

Friedel proved that the two crystalline forms of hexachloride of benzene are in accord with the well-known theory of their "*cis*" and "*trans*" arrangement (*Bull. Soc. Chim.*, 1891, [iii], **5**, 130). He developed the theory to show that tertiary symmetry is indicated for the *cis*- and binary for the *trans*-form. A calculation of the necessary ratio in which the two forms will be generated during saturation with chlorine and disruption of carbon bonds, compared with experimental results, confirmed the identification of each form.

This account would not be complete without a reference to the discussions between Friedel, Mallard, and Wyrouboff (*Bull. Soc. Miner.*, 1886, **9**, 121). Friedel insisted upon the capacity of crystallising together as a final test of isomorphism in opposition to views of Mallard, who was prepared to extend very widely the definition of isomorphous substances.

The *Bulletin de la Société de Mineralogie* contains a considerable number of Friedel's descriptions and measurements of mineral species.

Artificial Production of Minerals.—The synthesis of atacamite (*Compt. rend.*, 1873, **77**, 211), four years later than the thesis upon pyro-electric phenomena, was effected by the action of ferric chloride upon cuprous oxide in sealed tubes at 250°.

Friedel and J. Guérin (*Ann. Chim. Phys.*, 1876, [v], **8**, 24) studied various titanium compounds and obtained titanium sesquioxide in the form of rhombohedral crystals, isomorphous with oligist and ilmenite. Among the much disputed formulæ for the latter mineral, preference is given to $FeTiO_3$, in which iron and titanium are mutually replaceable as silicon can replace titanium in its higher stage of oxidation. Crystallised rutile was also obtained by the action of titanium chloride on ferrous oxide at a high temperature.

The publication of the most important series of syntheses was begun in 1879 (*Bull. Soc. Miner.*, **2**, 113). Most of the work done between

this date and 1887 was in collaboration with Edmund Sarasin and was published in full in the *Arch. Sci. phys. et natur. de Genève*, 1892.

The required materials, together with water, were heated in the very stout steel tube lined with platinum, already described. High pressure and a temperature of 500°, corresponding in the earth's crust to a considerable depth of rocky strata, were reached, and the results were interpreted with reference to geological theories. The use of a platinum tube guaranteed the purity of the compounds. The crystals produced within the few days devoted to an experiment were small and required care and skill in measurement to identify them with known species, but they were usually well defined and uniform in their aspect.

The first published observation of Friedel and Sarasin (*Bull. Soc. Miner.*, 1879, **2**, 113) described the formation of beautiful prisms of quartz with pyramidal terminations when an excess of amorphous silica was heated with caustic potash. These crystals, which are easily measurable, appeared frequently together with other minerals in later syntheses. Quartz with a new macle was observed among the crystals (*Bull. Soc. Miner.*, 1888, **2**, 29).

The formation of orthose feldspar (Friedel and Sarasin, *Bull. Soc. Miner.*, 1879, **2**, 158; 1880, **3**, 23; 1881, **4**, 171; *Compt. rend.*, 1881, **92**, 1374), under well defined conditions, threw new light upon the mode of formation of the so-called acid rocks. Friedel, with scrupulous care, repeated his experiments under various conditions during three years before he affirmed the absolute identity of the artificial and natural species. The materials were silicates of potassium and aluminium with a large excess of water. Quartz is usually formed as well, and when a higher temperature is employed tridymite also, showing that silica naturally crystallises in these two forms at corresponding temperatures. The bearing of these facts upon the mode of genesis of granite was pointed out.

Albite and analcime are formed by a similar process when sodium instead of potassium silicate is used. No intermediate feldspar containing the two bases could be obtained and the natural minerals having such a composition are probably mixtures (*Compt. rend.*, 1883, **97**, 290).

The action of alkalis and sodium silicate on the zeolites was investigated by Friedel and Sarasin (*Bull. Soc. Chim.*, 1884, [ii], **41**, 593). Friedel proposed a general formula for this mineral group and sought to verify it by transforming its different members. Sodium can be substituted for calcium in laumontite with formation of analcime. In this reaction, there is also formed a mineral nearly related to mesotype, and it was shown that the same mineral was

obtained by subjecting natural mesotype to the action of the same reagents.

Friedel, with his son, Georges Friedel, pursued a similar series of investigations upon the metamorphosis of mica. Many attempts were made to obtain white mica in presence of alkalis, but it was found that mica is not stable under these conditions, that at 400—500° it is easily decomposed by the alkalis, giving rise to other species, and when silicates or other salts are added the products of transformation resemble the well known series found at Somma.

When the micas are treated with alkalis alone, substitutions of one base for another could be obtained.

Muscovite (*Bull. Soc. Miner.*, 1890, **13**, 129), at 400—500°, in presence of dilute sodium hydroxide, is transformed without residue into fine crystals of nepheline, so pure that the constitution of this mineral could be definitely established as an orthosilicate, $AlNaSiO_4$. The transformation seems to consist in substituting sodium for potassium and hydrogen in muscovite without destroying the molecular arrangement. It was found impossible, however, to obtain a nepheline containing potassium without sodium. Mica is transformed into orthose by heating with potassium silicate and potassium hydroxide. Also, when a suitable proportion of silica was taken, a quadratic form of amphigene was produced without icositetrahedral grouping. This synthesis is interesting from a crystallographical point of view, because the form which appears at a temperature lower than that at which the mineral becomes cubic and isotropic shows parahemihedrism not recognised in natural specimens, and the pseudo-icositetrahedral form of the natural crystals is explained by a junction of three crystals with trirectangular axes.

Sodalite (*Bull. Soc. Miner.*, 1890, **13**, 180) was formed by heating mica with sodium chloride and hydroxide. It had the same composition, $3SiO_4AlNa + NaCl$, no matter what proportion of salt was added, and was identical with Somma sodalite.

Anorthite (*Bull. Soc. Miner.*, 1890, **13**, 230) can be obtained by heating mica with calcium chloride and hydroxide. The crystals are well formed, and free from potassium.

Mica is transformed by calcium hydroxide into a hydrated silicate of the cubic system not found in nature.

A mixture of sodium sulphate and hydroxide converts white mica into a new compound, $6SiO_4AlNa,Na_2SO_4,2H_2O$. The crystals are transparent, and isomorphous with those of nepheline, cancrinite, and microsommite. A mineral like the preceding, but with one molecular proportion of water, is formed in small quantity, also a little black mica. Muscovite mica, heated with sodium carbonate and hydroxide, gives a mineral like cancrinite, $6AlNaSiO_4,Na_2CO_3,2H_2O$.

Friedel and Sarasin (*Bull. Soc. Miner.*, 1887, **10**, 737), prepared topaz by heating aluminium fluorosilicate. Quadratic crystals of aluminium fluoride are also formed. Friedel pointed out an error in the usual method of analysing topaz, arising from a loss of aluminium fluoride, as well as silicon fluoride, when the mineral is heated in a platinum crucible. The composition, instead of being variable, as was supposed, is constant, and corresponds with that required for the formula $Al_2F_2SiO_4$.

The following list comprises other syntheses of minerals achieved by Friedel and Sarasin: Libethenite (*Bull. Soc. Miner.*, 1879, **2**, 157); hopeite (*ibid.*, 153); copper selenite (*ibid.*, 1881, **4**, 176); phosgenite (*ibid.*, 176); leadhillite (*Bull. Soc. Chim.*, 1883, [ii], **39**, 626); calcite (*Bull. Soc. Miner.*, 1885, **8**, 304); mellite was synthesised by Friedel and Balsohn (*Bull. Soc. Miner.*, 1891, **14**, 26); and Friedel prepared cumengeite (*Bull. Soc. Miner.*, 1892, **15**, 96), bolcite (*ibid.*, 1894, **17**, 6), and martite (*ibid.*, 1894, **17**, 150).

From an examination of diamonds contained in native iron from Cañon Diablo (*Compt. rend.*, 1893, **116**, 224), Friedel concluded that their formation had been accompanied by that of sulphide of iron at a relatively low temperature. He attempted to obtain crystallised carbon by the action of sulphur on a highly carburetted cast iron at 450—500°. A black powder was obtained hard enough to scratch corundum, but in too small quantity to be analysed. This essay is particularly interesting, as it seems to imitate a natural process.

The following new species of minerals were discovered by Friedel: Wurtzite (*Compt. rend.*, 1861, **52**, 983); adamine (*Compt. rend.*, 1866, **62**, 692); and delafossite (*Compt. rend.*, 1873, **77**, 211); whilst carnotite was described by Friedel and Cumenge (*Bull. Soc. Miner.*, 1899, **22**, 26).

The *Bulletin de la Société de Mineralogie* from 1879 to 1894 contains numerous descriptions of minerals from different localities. Many of these investigations were made by Friedel in connection with his duties as Curator of the Mineralogical Cabinet of the School of Mines, which led him constantly to examine minerals from new localities, and he was at all times actively employed in adding new specimens to that fine collection.

L. F. Nilson

NILSON MEMORIAL LECTURE.

(Delivered on July 5th, 1900.)

By Otto Pettersson, Professor of Chemistry in the University of Stockholm.

Lars Fredrik Nilson, born in Ostergothland in 1840, received his education at the high school of Wisby, on the island of Gothland, where his father possessed a large farm, Rosendal. The beautiful scenery and luxuriant vegetation of the sunny island in the Baltic, as well as the historical traditions attaching to its grand mediæval monuments now in ruins, left an impression upon the boy's mind never forgotten in after life. It is, in fact, impossible to understand the character and life-work of Nilson without taking into account his ardent attachment to the island where his youth was spent. As a chemist, he devoted himself with predilection to such investigations as had a bearing upon the development of the great but neglected agricultural resources of Gothland. I shall have more to say of this later; suffice it here to mention that the sugar industry, now so flourishing, and the cultivation of the sugar beet on that island were introduced on his initiative. Still Nilson had no leaning towards commerce; like the true man of science he was, he contented himself with being the adviser and promoter of economic progress. Although his occupations in Stockholm only allowed him time to make a short visit yearly to Gothland, yet he retained until the end of his life the management of a little farm there, which was his inheritance or patrimony, his part of the ancestral soil.

In 1859, at the age of 19, Nilson became a student at Upsala, his studies being directed towards biological science, especially zoology and geology, for which he obtained high marks in the examinations. Although his mineralogical study compelled him to acquire some knowledge of chemistry, he seemed at that time to entertain no special predilection for it. This work, however, brought him into personal contact with the director of the chemical laboratory of the University, Lars Fredrik Svanberg, whose well-known research upon molybdenum was carried out in conjunction with Struve in 1848 in Berzelius' laboratory in Stockholm. Svanberg had been a military engineer until Berzelius, who recognised his great ability as a mineralogist and his extraordinary analytical skill, offered him a place in his laboratory. Their acquaintance soon deepened into a lasting friendship, and greatly did the old master of science need the support of his strong-minded friend in the last critical years of his life, when his system of chemis-

try, once so firmly established, seemed to be on the point of giving way, attacked as it was from all sides by the advocates of the metaleptic and type theories.

After Berzelius' death, Svanberg was nominated Professor of chemistry in Upsala (1853), and entrusted with the task of erecting a new institution with laboratories for chemistry, mineralogy, and physics. His aim was to raise the study of chemistry at the University, which had flourished under Torbern Bergman, but during the succeeding sixty years had become utterly neglected. This was not easy to accomplish, although Svanberg in many respects possessed excellent qualifications for it; he had an ardent and unselfish devotion to his science, he owned the greatest collection of chemical literature ever possessed by a private person in Sweden, and his phenomenal memory embraced the entire development of chemical science from the first beginning of a rational theory until the time of Berzelius' death. Bearer of the great traditions of the Berzelian era, he, however, had not the power of carrying to victory the ideas which he had defended in company with his illustrious friend.

The question pending at that time was the constitution of the organic bases and acids. Berzelius and Svanberg interpreted both as combinations of an inorganic base or acid with an organic compound, which played the part of 'copula.' Examples of such coupled combinations were to be found also in inorganic chemistry. The first ammoniacal platinum base discovered by Magnus was platinous chloride coupled with ammonia.* Ethylamine, in the words of Berzelius, was "mit ætheren gepaartes Ammoniak."† In close analogy to hydrofluosilicic acid, which was interpreted as hydrofluoric acid coupled with silicon fluoride, $2HF,SiF_4$,‡ acetic acid was regarded as a copula of oxalic acid with ethane, trichloroacetic acid, a copula of oxalic acid with carbon sesquichloride, &c.

It seemed, in fact, to be a desperate position to uphold the apparently extravagant formulæ

$$C_2H_6C_2O_3 + H_2O$$

and

$$C_2Cl_6C_2O_3 + H_2O$$

against the great generalisations of the type theory of Dumas and Williamson expressed in the symbols

$$\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O \qquad \left.\begin{matrix} C_2Cl_3O \\ H \end{matrix}\right\} O.$$

Still there was in Berzelius' formulæ, in spite of their errors with regard to atomic weights and to the part played by water in the

* $PtClNH_3$ according to Berzelius. † $NH_3C_4H_4$, according to Berzelius.

‡ $3HF,2SiF_3$, according to Berzelius.

constitution of the acid, a germ of truth, and a possibility of progress which the type formulæ lacked. It was Kolbe who was destined to bring out the whole purport of Berzelius' conceptions concerning the copulated organic compounds. In a classical investigation executed partly in Playfair's laboratory in London, and partly in Bunsen's laboratory in Marburg, Kolbe, in 1849, the year after Berzelius' death, proved that acetic acid by electrolysis gave birth to ethane, carbonic acid, and hydrogen * (*Annalen*, 1849, **69**, 252). The further steps of progress from Berzelius' and Kolbe's point of view to that of the modern theory of organic chemistry were the synthesis of sodium propionate by Wanklyn,

$$C_2H_5Na + CO_2 = C_2H_5 \cdot CO_2Na,$$

and the brilliant discovery of the valency of the elements by Frankland.

From the date of Berzelius' death, Svanberg abandoned experimental work, feeling that his mission was to organise the teaching of chemistry on a broad basis in the new laboratory of the university, and to arouse interest in the study of his science. Like the seer of old, he was content to show to the next generation of his people the path into the land of promise. There can be no doubt that he succeeded, for most of the chemists who now hold the position of teachers at our academies or leaders of the industrial or metallurgical works of our country are pupils of Svanberg. The names which will be most familiar to you are Cleve, Nilson, and De Laval the reformer of the dairy industry of the world.

In 1865, Nilson was ready to take his degree. The examination regulations in Sweden are somewhat complicated, being specially drawn up with a view of insuring that the claims of the humanities shall not be subordinated to those of empirical science; the candidates for the Doctorate of philosophy, therefore, were obliged to undergo examinations in history, philosophy, languages, &c., in addition to their chief subject. The examination itself was a mere formality, but it was preceded by private examinations in every subject, and all these had to be passed within a certain time, usually six months, previous to the day of examination, if not, the whole procedure had to be repeated. Nilson was ready for examination when bad news arrived from home. His father had had a stroke of apoplexy, and the work on the farm was much impeded by his illness. Nilson himself was at that time very delicate in health, suffering from bleeding from

* It scarcely needs to be mentioned that neither Berzelius nor Kolbe then distinguished between the radical methyl and the compound dimethyl or ethane, the distinction being first made by Frankland several years afterwards.

the lungs. To leave Upsala some weeks before the examination meant to postpone it for a year, or indeed for ever, uncertain as it was if he could hope to return any more. Nilson, however, did not hesitate; he went over to Gothland, and undertook the management of the farm, himself labouring in the fields. When his father, some months afterwards, recovered, to the happy astonishment of the family, Nilson could inform him of two things: firstly, that the harvest was in the barns in the best condition, and the soil prepared and sown for the autumn; secondly, that he had succeeded without any technical assistance in installing the engine and threshing machinery which had just arrived from England—the first machinery of that kind to be introduced into Gothland—and that it had worked excellently. "This" —Nilson wrote to a friend—"awakened the liveliest astonishment in my father." Shortly afterwards Nilson returned to the university, where a richer harvest was ripening for him.

He returned another man than he went. The healthy country life, and labour with its responsibilities and its success had changed the sickly youth, overburdened with mental exertion and doubt about his capacities and calling in life, into a strong, resolute man who knew his aim and how to realise it:

"Der Riese hat die Mutter Erde berührt"
"Und es wachsen ihm neu die Kräfte."

From that time until thirty-two years afterwards, when he literally broke down under the burden of labour, he was never ill, and never tired. Without any difficulty, he passed his examination, obtained his degree with a dissertation on thialdine, and a year later became head of the laboratory as chief assistant and demonstrator of chemistry.

A few words concerning the laboratory of Upsala thirty to forty years ago may not be out of place. There was the large and very crowded common laboratory room irreverently called "the stable" by the students on account of the composition of its atmosphere in which free ammonia entered in a not inconsiderable proportion. Nilson here appeared as a calm and patient teacher rather sparing of words, preferring to give an experimental demonstration or practical advice instead of long verbal explanations. Inside was the assistants' room and Svanberg's private laboratory, where those occupied with scientific investigations had places. Everything here reminded one of Berzelius. There were the balances, the blowpipes, the platinum crucibles—some of the first ever made—that had belonged to him. On the shelves there were some of his preparations, venerable relics from the days of his discovery of selenium, thorium, &c. At a certain hour of the day Svanberg appeared in his old military coat—the abomination of his

august colleagues of the academical *consistorium majus*—eager to know the progress of every new experiment, himself the most enthusiastic of all when success attended the endeavours of his pupils. His rooms on the floor above the laboratory were lined with bookshelves containing thousands of volumes arranged in double rows on each shelf. These treasures of the chemical literature of bygone centuries were destined to belong to the University after his death, and were at the disposal of his assistants and pupils during his lifetime. The circle of scientific students in Svanberg's laboratory was united by ties of friendship in the hours of labour and of pleasure. As work usually continued until late in the evening, there seemed to be little time left for pleasure, but the balance between work and pleasure was kept up in another way. Whilst it was customary in the private laboratory where Nilson presided to enliven the hours of work with conversation, anecdotes, puns, occasionally by a song, &c., it was considered unfitting to introduce scientific matters into the conversation of leisure hours. Nilson positively did not admit it, and woe to him who dared to speak of political or philosophical matters when Nilson intended to be merry. And he was always merry when he was with his friends, the merriest of them all. He had a thousand devices for putting a stop to a conversation which threatened to take a tiresome turn. He would, for example, sit listening for a while with a grave face, and then interpose with a short nonsensical observation, delivered with great solemnity in the accents of some political or scientific worthy of pedantic fame, while a gleam of fun shot forth from under his heavy, dusky eyebrows. The effect was irresistibly comic, so much the more as it came unforeseen. His hearers were at first puzzled, then one chuckled, another laughed, and in a minute the impending political or philosophical discourse was drowned in a chorus of laughter in which Nilson's voice at last joined in accents swelling like big waves and rollers of an ocean of mirth.

Out of the great number of scientific researches undertaken by Nilson, I will speak only of some of the most important, in order to show what scientific impulses he received and how his life-work is connected with the work of the leading masters of his science in present and bygone ages.

In 1871, his first paper in inorganic chemistry "On the Sulphides of Arsenic" was published in the *Proceedings* of the Royal Academy of Sciences in Stockholm. This research was undertaken in order to complete the investigation upon sulphides and sulpho-salts which Berzelius had commenced in 1821—1826.

This period represents the most brilliant epoch in the history of Berzelius, when his generalising genius shone forth in its full vigour,

and made him for a time the undisputed authority on chemical theories. Until that time he had been an adversary of the conception of the binary composition of haloid salts, but in 1821 he at last admitted the cogency of the experimental proofs furnished by Sir Humphry Davy and Gay-Lussac of the elementary nature of the halogens and the binary composition of their hydrogen compounds HCl, HF, &c. His mind was then opened to a wider view of the nature of inorganic compounds which embraced all kinds of salts, and resulted in a new classification of the elementary and compound substances constituting the realm of inorganic chemistry. In Berzelius' Annual Report for 1826, his system of classification is enunciated in short and pregnant definitions: Elements are either positive (metallic) or negative (non-metallic).

Among the non-metallic elements are the two groups:

(1) Halogens * (*Corpora halogenia*) which form binary saline compounds with the positive metals, and,

(2) Amphids † (*Corpora amphigenia*) which form basic compounds with positive and acid compounds with negative elements.

Berzelius says: "There are three classes of salts. The first class, which I denote as *haloid* salts, are combinations of an electro-positive metal and a halogen. The second class, which I denote by the name of *amphid* salts, are constituted of one base and one acid. There are four different amphid salts: oxy-salts, sulpho-salts, selenium salts, and tellurium salts. When we consider the influence this classification has exercised on the theory and the teaching of inorganic chemistry during the greater part of the nineteenth century, we can judge of the enthusiasm which greeted it at the time of its first appearance. Svanberg, however, considered that the analogies which Berzelius had found to exist between the salts of the amphid group needed elucidation and to some extent correction. At his suggestion Nilson undertook the study of the selenium salts and sulpho-salts, of which Berzelius had synthetically prepared 120 without, however, being able to enter upon a closer study of more than a small number of them.

According to Berzelius, there existed three kinds of arsenical sulpho-salts, namely, sulpharsenates, sulpharsenites, and hyposulpharsenites, and four sulphides, namely, As_2S_5, As_2S_3, As_2S_2, and As_6S. Nilson showed that the hyposulpharsenites, as well as the sulphide As_6S, do not exist. The red or brown precipitate which separates out from boiling solutions of the trisulphide As_2S_3 in sodium carbonate consists of impure realgar, As_2S_2, and the black sulphide, As_6S, which was supposed to arise from the decomposition of realgar with alkali, is a mixture of this substance with arsenic. He synthesised realgar in a number of different ways,

* Chlorine, iodine, fluorine (according to Berzelius, 1826).

† Oxygen, sulphur, selenium, and tellurium.

and found that this sulphide is liable to decomposition in air, whereby arsenic trisulphide, As_2S_3, and arsenic trioxide, As_2O_3, are formed,

$$3As_2S_2 + 3O = 2As_2S_3 + As_2O_3.$$

This change seems to throw some light upon the genesis of orpiment in nature by metamorphosis and decomposition of realgar. In fact, orpiment seems to be a secondary product, since almost every crystal of realgar is found to be coated with a bright yellow deposit of the trisulphide, which increases in bulk with time. Of real sulpho-salts of arsenic derived from the tri- and penta-sulphide, Nilson synthesised a great number. Likewise he discovered the existence of new oxysulphides ($As_2S_2O_3$) and oxysulpho-salts of arsenic.

Nilson's next work, "Researches on the Salts of Selenious Acid," (*Nova Acta Reg. Soc. Ups. III*, 1875), may also be regarded as a complement to the work of Berzelius. In 1817, Berzelius discovered selenium and selenious acid,* of which he described a number of salts. For the most part he did not go beyond qualitative experiments, and only rarely stated the quantitative composition of a few salts (of sodium, barium, lead, silver) with a view of ascertaining the basicity of the new acid. Nilson considerably enlarged our knowledge of the neutral and acid combinations of selenious acid by accurate analyses of more than one hundred of its salts.

In the beginning of the seventies a new era dawned for inorganic chemistry with the discovery of the periodic relations of the elements by Newlands, Mendeléeff, and Lothar Meyer. The natural system of Mendeléeff in which the new idea for the first time had found its fullest and most perfect expression, completed and supplanted Berzelius' classification of the elements just as the natural system of plants by Jussieu had supplanted the Linnæan system of the vegetable kingdom. Moreover, the periodic law as promulgated by Mendeléeff invited experimental inquiry. There were new elements to discover, atomic weights to correct, elements of doubtful chemical character to study.

The crucial test of the periodic law seemed to lie with the elements of the rare earths. As these elements until then had been found to exist almost exclusively in Scandinavian minerals in which the oxides yttrium, erbium, terbium, cerium, lanthanum, didymium, and thorium had been discovered by Gadolin, Berzelius, and Mosander, it seemed incumbent upon the Swedish chemists to take up the intricate problem once more. Cleve and Höglund undertook a research upon yttrium, thorium, and erbium, which inaugurated the well-known series of investigations still being carried on by Cleve and his pupils.

Shortly afterwards Nilson began the study of the rare earths con-

* "Selenic" acid in the terminology of Berzelius.

tained in euxenite, of which mineral he had received a considerable quantity from Professor Waage in Christiania. He soon succeeded in extracting a large quantity of the crude oxides, and these were submitted to the fractionating process invented by Berlin, and afterwards practised by Bahr and Bunsen, namely, heating the nitrates until partially decomposed. Nilson began this work with a special purpose in view. He and I had agreed to make a research in common upon the physical and chemical constants of such elements and compounds of the rare earths as were considered to have a special bearing upon the periodic law of Mendeléeff. The material for this investigation was to be partly beryllium oxide, which we prepared in common from crude beryl, and partly such oxides of the rare elements as Nilson hoped to separate in the purest possible condition from the euxenite oxides by systematic fractionation.

The bivalency of beryllium, with the atomic weight 9·2, was a cardinal point of the periodic law. The existing experimental determinations of the atomic heat of metallic beryllium seemed to confirm this view, since the specific heat was found to be 0·642 which, if Be = 9·2, makes the atomic heat 5·9 in accordance with the criterion of Dulong.

Nilson and I prepared metallic beryllium from equivalent quantities of beryllium chloride and sodium heated to redness in an hermetically closed crucible of wrought iron. The metal thus obtained had a specific heat 0·41, or only two-thirds of that formerly found, a value which agrees far better with the view that the element is tervalent with an atomic weight of about 13·8, contrary to the requirements of the periodic law.

Still the question of the real atomic weight and valency of this element could be considered open to doubt, since there existed the possibility that beryllium might be an exception to the rule of Dulong, like carbon, boron, and silicon, and that its specific heat would be found to increase with temperature. This explanation received support from a remarkable discovery by Brögger and Flink, who, on examining the crystallised metal prepared by us, found it to possess the same crystalline type (of the hexagonal system) as the bivalent metals, magnesium, zinc, and cadmium. We resolved therefore to determine the specific heat of the metal at higher temperatures than 100°, and also the vapour density of its chloride, in order to finally decide the chemical character of the element.

We found that the specific heat increases rapidly with rise of temperature, from 0·42 between 100° and 0° to 0·50 between 300° and 0°. Professor Humpidge, of Aberystwyth, who, immediately afterwards, with great experimental skill revised the physical constants of this element, arrived by other methods than ours at concordant results.

The following table contains the numbers thus found representing the atomic weight and specific heat of beryllium :

Atomic weight = 9·081 (H = 1), Nilson and Pettersson (*Ber.*, 1880, **13**, 1451 ; 1884, **17**, 987), = 9·027 (H = 1), Krüss and Morath (*Annalen*, 1890, **262**, 38).

Density *d* 20°/20° = 1·85, Humpidge (*Proc. Roy. Soc.*, 1885, **39**, 4).

Specific heat :

Temperature.	Nilson and Pettersson. Ice-calorimeter.	Temperature.	Humpidge. Method of mixtures.
0—100°	0·4246	11—100°	0·4286
		11—145	0·4515
		11—193	0·4696
0—300	0·5060	15—240	0·4885
		14—312	0·5105
		11—360	0·5199
		17—447	0·5403

The vapour density of the chloride was found to be (Nilson and Pettersson) :

Temperature.	Density.	Temperature.	Density.
490°	6·700	745°	2·753
520	4·174	812	2·793
589	3·067	1080	2·684
597	3·031	1115	2·779
604	3·090	1184	2·824
686	2·853	1502	2·791
720	2·926		

As the determination of the vapour density of this chloride was the first of a great series of similar experiments, a few words about the methods employed may find a place here.

The determination of vapour densities at high temperatures was at that time (1880—1890) a matter of unusual interest to chemists, since Victor Meyer (1876) had improved the experimental technique by introducing the principle of displacement (Luftverdrängungsverfahren), devised by Dulong (compare Dumas, *Compt. rend.*, 1874, **78**, 536) into use in a practical and elegant form. Although this method led Meyer and his pupils to some of the most important discoveries of that time, among which the breaking up of the molecules of the halogens at high temperatures was the most remarkable, his method was by no means adapted for accurate measurements. The methods which we employed in the determination of the vapour density of beryllium chloride and subse-

quent experiments with the chlorides of aluminium, indium, germanium, gallium, &c., were described in a paper entitled "Ueber ein neues mit exacter Temperaturbestimmung verbundenes Verfahren zur Feststellung der Dampfdichte flüchtiger Körper" (*J. pr. Chem.*, 1886, [ii], **33**, 1). The platinum vessel in which the chloride was allowed to evaporate also acted as the bulb of a gas thermometer of the compensatory type devised by me (*J. pr. Chem.*, 1882, [ii], **25**, 102). In our experiments with beryllium chloride and other metals, we found it to be an indispensable condition for obtaining constant results (1), to prepare the chloride from the pure metal by means of dry hydrogen chloride; (2), to employ platinum tubes for the preparation of the chloride and platinum bulbs for the density determination; (3), to evaporate the substance in an atmosphere of an absolutely dry indifferent gas (usually carbon dioxide).

In beryllium chloride, as in most other volatile substances, there seems to exist at low temperatures an unstable association of molecules. For the study of this transitory state, the displacement method of Dulong—V. Meyer is not sufficient, and must be supplemented by that of Dumas. We employed for determinations of the vapour density of chlorides, &c., at such temperatures the modification of Dumas' method introduced by O. Pettersson and G. Ekstrand (*Ber.*, 1880, **13**, 1191). From 730° upwards, beryllium chloride was found to have almost exactly the constant density 2·77, as calculated for the molecule $BeCl_2$.

While the beryllium work was proceeding, important discoveries had been made in the chemistry of the rare earths. The mineral samarskite from N. America was found to contain, besides the element terbium already announced by Mosander,* a whole group of new elements. The first discoveries of these earths were due to Delafontaine in 1878. The confusion about the names, the atomic weights and characteristic absorption bands of the new elements of the samarskite group, which at first appeared in the descriptions given by Delafontaine, Laurence Smith, and others, gradually subsided under the critical scrutiny of Roscoe, Soret, Lecoq de Boisbaudran, and Marignac.

Moreover, the gadolinite group of earths, which was considered until then to contain only two elements, yttrium and erbium, began to break up into a number of new earths. Soret had announced the existence of a new element, X (later identified with the holmium of Cleve) rich in absorption bands, and Cleve found that the bands of the erbium of 1873, of the atomic weight 170·5, began to split up into one group belonging to an element forming a red oxide with the characteristic emission spectrum (by incandescence) of the old erbium, and another group of only two absorption bands in the visible spectrum

* Mosander's denomination for this element was "erbium."

belonging to a colourless oxide, to which he later gave the name thulium. The most promising discovery was, however, due to Marignac, who in 1878 found that the entire group of absorption-bands of the erbium earths could be eliminated by successive fractionating, whilst the atomic weight of the remaining oxide increased. He justly concluded that a new element of high atomic weight (172·5) must exist, which he denominated ytterbium. From want of material, he could not purify and isolate its oxide; he therefore exhorted such chemists as possessed a greater supply of material to continue the investigation of the new earth. Now it became Nilson's turn to earn the reward of his long labour; he had started his work with a greater quantity of raw material than other chemists of that time, and he had worked, as was his wont, in the most methodical manner. Moreover, the material, oxides from euxenite, which he treated was singularly rich in the elements of higher atomic weight of the gadolinite group of earths. The consequence was that he could fractionate easily a considerable quantity of nitrates up to the point indicated by Marignac, where the absorption-bands began to vanish, and the atomic weight of the metal amounted to 172·5. Before he had reached that point, however, Nilson made the startling observation that there separated out, among the insoluble basic salts, the nitrate of a less basic metal of lower atomic weight. The equivalent weight of the oxides in the insoluble part of the decomposing nitrates had a tendency to sink instead of to rise. He immediately concluded that, together with ytterbia, a new oxide must exist. The atomic weight of the elements contained in these fractions rapidly sank to 134, and even lower, whilst the atomic weight of the element in the other part of the fractions slowly rose to 173·01, the oxide became snow-white, and all absorption-bands vanished from the solutions of its salts. Nilson thus had succeeded in isolating two of the best defined elements of the rare earths, ytterbium (*Ber.*, 1879, **12**, 550) and scandium (*ibid.*, 554). Both are characterised by brilliant emission spectra studied by R. Thalén, and by highly interesting chemical properties. Both elements fill prominent places in the third group of the periodic system, and scandium is especially remarkable, as it is identical with Mendeléeff's hypothetical element ekaboron.

The intention of Nilson and Pettersson to isolate the elements of such oxides as could be obtained in a state of chemical purity from the rare earths and determine their physical and chemical constants was not to be fulfilled. In 1881, I was called to undertake the duties of Professor of chemistry at the newly instituted Stockholms Högskola, Nilson remaining in Upsala as Professor of analytical chemistry. Before parting, we found time to determine the specific volume and heat of the oxides and sulphates of all earth-metals then known (*Ber.*, 1880, **13**, 1459).

Occupied as he was with the discovery of ytterbium and scandium, Nilson still found time to publish some important researches upon the chemistry of other members of the rare elements.

Already, in 1877 (*J. pr. Chem.*, [ii], 15, 177), he had taken up the study of the platinichlorides of these elements commenced by Cleve, Jolin, and others.

The platinichlorides are of three general types:

A. $\left\{\begin{matrix} 2RCl,PtCl_4 \\ RCl_2,PtCl_4 \end{matrix}\right\}$ (normal platinichlorides).

B. $RCl_3,PtCl_4$ ($\frac{2}{3}$ „ „).

C. $RCl_4,PtCl_4$ ($\frac{1}{2}$ „ „).

To A belong the salts of uni- and bi-valent metals, such as potassium, barium, &c. The platinichloride of beryllium, $BeCl_2,PtCl_4,8H_2O$ (Marignac and others), belongs to this type.

To B belong the platinichlorides of the tervalent elements, aluminium, chromium, iron (Nilson), didymium, erbium, cerium, lathanum (Cleve, Jolin, and others). Yttrium and indium are exceptions, their platinichlorides being represented by the formulæ $4YCl_3,5PtCl_4,52H_2O$ (Cleve, Nilson), $InCl_3,5PtCl_4,36H_2O$ (Nilson).

Of the type C ($\frac{1}{2}$-normal platinichlorides), only one member was known, namely, the thorium salt, $ThCl_4,PtCl_4,12H_2O$, described by Cleve. Nilson found that the quadrivalent metallic elements as a rule form platinichlorides of this type, for example:

$$SnCl_4,PtCl_4,12H_2O.$$
$$ZrOCl_2,PtCl_4,12H_2O.$$

The platinichlorides of metallic elements thus furnish a very characteristic indication of their valency.

The same holds also to a certain extent with regard to the platinochlorides, a class of compounds which, before Nilson's time, had been very little studied. Nilson prepared (*J. pr. Chem.*, 1877, [ii], 15, 260) the corresponding chloroplatinous acid,

$$H\cdot Cl:Cl\cdot Pt\cdot Cl:Cl\cdot H,$$

which exists only in dilute solution, and on evaporation in a vacuum decomposes, losing hydrogen chloride forming the compound $H\cdot Cl:Cl\cdot PtCl$, which at 100° is transformed into platinous chloride, $PtCl_2$.

From the same year (1877), dates an important research upon plato- and diplato-nitrites. The constitution of the platonitrites, first studied by Lang (*J. pr. Chem.*, 1861, 83, 415), had been interpreted by Blomstrand (*J. pr. Chem.*, 1871, [ii], 3, 186) to be

$$RO\cdot NO:NO\cdot OPt\cdot O\cdot NO:NO\cdot OR,$$

or compounds of platotetranitrosylic acid.

The platonitrites are beautifully crystallised salts. Nilson found that in some cases they decompose into diplatonitrites, nitrous acid, and nitrites (*Ber.*, 1876, **9**, 1722).

$$2\begin{matrix}\mathrm{RO{\cdot}NO{:}NO{\cdot}O}\\\mathrm{RO{\cdot}NO{:}NO{\cdot}O}\end{matrix}\!\!>\!\mathrm{Pt}=\begin{matrix}\mathrm{RO{\cdot}NO{:}NO{\cdot}O{\cdot}Pt}\\\mathrm{RO{\cdot}NO{:}NO{\cdot}O{\cdot}Pt}\end{matrix}\!\!>\!\mathrm{O}+\mathrm{N_2O_3}+2\mathrm{NO{\cdot}OR}.$$

In this way, the diplatonitrites of silver, beryllium, and iron (Fe‴) are formed. The tervalent metals, yttrium, erbium, lanthanum, and didymium form normal platonitrites of the composition

$$\mathrm{R_2(4NO_2Pt)_3}+9 \text{ or } 18\mathrm{H_2O}.$$

Nilson found that the platonitrites of potassium and barium are changed into iodoplatonitrites (*Ber.*, 1878, 11, 879) if treated with iodine in alcoholic solution. This new class of salts occupies an intermediate position between the platonitrites and platinoiodides.

$$\begin{matrix}\mathrm{R{\cdot}O{\cdot}NO{:}NO{\cdot}O}\\\mathrm{R{\cdot}O{\cdot}NO{:}NO{\cdot}O}\end{matrix}\!\!>\!\mathrm{Pt}\ \text{(platonitrites)}.$$

$$\begin{matrix}\mathrm{R{\cdot}O{\cdot}NO{:}I}\\\mathrm{R{\cdot}O{\cdot}NO{:}I}\end{matrix}\!\!>\!\mathrm{Pt}\ \text{(platoiodonitrites)}.$$

$$\begin{matrix}\mathrm{RI{:}I}\\\mathrm{RI{:}I}\end{matrix}\!\!>\!\mathrm{Pt}\ \text{(platinoiodides)}.$$

In 1882, Nilson published his first researches upon thorium which he later completed in conjunction with G. Krüss (*Zeit. physikal. Chem.*, 1887, 1, 301). He succeeded in obtaining metallic thorium and determining the vapour density of its chloride.

In preparing pure thoria, Nilson experienced the difficulty of removing from it the last traces of cerium dioxide, which most pertinaciously clings to it. The fact that this was successfully overcome in 1883 has been of some importance in the industrial rivalry of the great incandescent lighting companies, since the first patent claimed the employment of pure thoria, which is, however, by no means a fit material for incandescent lamps.

Nilson and Krüss (*Zeit. physikal. Chem.*, 1887, 1, 391) also tried to isolate niobium from potassium fluoroniobate, but, like Marignac, they obtained the hydride, NbH, instead of the metal. The specific heat of this hydride was found to diminish considerably with rise of temperature, as shown by the following numbers:

Temperature	0—100°	0—210°	0—301°	0—440°
Spec. heat of NbH.....	0·0977	0·0925	0·0871	0·0834
Molecular heat of NbH...	9·3	8·8	8·3	7·9

In the course of his long work upon the elements of the rare earths, Nilson had acquired a rich collection of their oxides, extracted from

different minerals. When Nilson and Krüss (*Ber.*, 1887, **20**, 3067) spectrometrically compared the relative intensity of the characteristic absorption-bands of holmium, thulium, didymium, erbium, samarium, &c., in the solutions of basic nitrates of oxides derived from different minerals, they discovered remarkable variations, similar in character to those observed in 1886 by Crookes (*Proc. Roy. Soc.*, 1886, **40**, 563) who stated that it was possible to eliminate band after band from the original didymium spectrum until only a single band λ 443 was left. From similar observations, Nilson and Krüss drew the following conclusion : "Nach obigen Auseinandersetzungen hätten wir an Stelle des Erbiums, Holmiums, Thuliums, Didyms, und Samariums, die Existenz von mehr denn zwanzig Elementen anzunehmen."

Few chemists of the present day will admit the strictness of this conclusion. There are many facts indicating that absorption bands as well as luminous bands of fluorescence cannot be regarded as essential characteristics of elementary substances. The experiences of Sorby with jargonium, as well as the observations of Liveing upon the variations occasioned by the nature of the solvent, and by impurities, on the intensity of absorption bands, are instructive in this respect. We can also hope that the study of the radio-active substances which are found to accompany the rare elements may throw light upon this question, so that the nebula of elementary matter which now seems to exist within the erbium and other groups will dissolve into well-defined elements.

Once more, after Nilson had taken up his residence at Stockholm as Professor of agricultural chemistry, an opportunity arose for carrying on the investigation upon the physical and chemical properties of the rare elements which we had planned in earlier days. The time for our joint work was, however, very limited owing to official duties, and the fact that new scientific interests had arisen on both sides. Nilson's efforts were concentrated upon the problems of augmenting the harvests and the fertility of the soil, whilst mine were concerned with the physical and chemical properties of the ice and water of the ocean. Still, we were able to spare about three weeks every year for research, and of these we made five by working late.

Much uncertainty prevailed with regard to the formulæ and molecular weights of the chlorides and similar compounds of aluminium, indium, gallium, iron (Fe'''), and chromium. The vapour densities of aluminium chloride and ferric chloride had been found by Deville and Troost (*Ann. Chim. phys.*, 1860, [iii], **58**, 283) as well as by V. Meyer (*Ber.*, 1879, **12**, 1199) to correspond with those required for the formulæ Al_2Cl_6 and Fe_2Cl_6, whilst indium chloride, according to V. Meyer, must be represented by the formula $InCl_3$. About gallium chloride opinions were divided, Lecoq de Boisbaudran's determinations (*Compt. rend.*, 1881, **93**, 329) being in accordance with the

doubled formula Ga_2Cl_6, Friedel's (*ibid.*) more with $GaCl_3$. The question seemed the more ambiguous as the determinations according to Dumas' method always seemed to give greater values for the density than those obtained on Dulong's principle at the same temperatures.

We found that no range of temperatures exists through which the vapour density of these chlorides is sufficiently constant to warrant the doubled formulæ Al_2Cl_6, In_2Cl_6, &c. Whilst the density of aluminium chloride as observed by Deville and Troost is 9·20 between 350—440° (corresponding with that required for the formula Al_2Cl_6), it increases below that temperature, and decreases above it (*Zeit. physikal. Chem.*, 1889, 4, 206) until at about 800° (or even below that temperature, if evaporated in an indifferent gas) the value 4·60* is obtained which remains constant for some hundred degrees.

The vapour of aluminium chloride at low temperatures—like that of acetic acid studied by Cahours—consists of unstable associations of molecules, $n AlCl_3$, which generally undergo dissociation into $AlCl_3$ as the temperature increases. This dissociation depends, not only upon temperature, but also upon pressure, consequently dissociation will be found to be more advanced at a certain temperature if the chloride is evaporated in an atmosphere of an indifferent gas, as is the case in experiments with the displacement method. This accounts for the discrepancy between the vapour densities determined on Dumas' and on Dulong's principles (*Zeit. physikal. Chem.*, 1889, 4, 224).

At very high temperatures we observed a gradual breaking up of the molecules of these chlorides, characterised by a slight diminution of the vapour density. The temperature at which this chemical dissociation begins is very different in different chlorides, for while beryllium chloride maintains its normal vapour density 2·77 up to 1500—1600°, aluminium chloride begins to show signs of chemical dissociation above 1000°, and gallium chloride below this.

We found that indium has three chlorides: $InCl_3$, $InCl_2$, InCl (Trans., 1888, **53**, 814; *Zeit. physikal. Chem.*, 1888, 2, 65), and gallium two chlorides: $GaCl_3$ and $GaCl_2$, each characterised by the normal vapour density required for the respective formulæ. Thus it is proved that a metal such as indium can exist in gaseous compounds as a uni-, bi-, and ter-valent element.

In 1886, Clemens Winkler discovered germanium, the ekasilicon of Mendelćeff, and entrusted to us the determination of its physical constants, namely, the specific heat of the metallic element and the vapour density of its chloride, $GeCl_4$, and sulphide, GeS. The results of this investigation are published in 1887 in a paper entitled: "Ueber

* The theoretical value for $AlCl_3$ is 4·60.

einige physikalische Constanten des Germaniums and Titans" (*Zeit. physikal. Chem.*, 1887, **1**, 27).

From 1878 to 1883, Nilson filled the position of Professor of analytical chemistry at the University of Upsala. In 1883, he became Professor of agricultural chemistry at the Royal Academy of Agriculture in Stockholm. He devoted himself to his new duties with the same energy and interest which he had shown in his investigations in theoretical chemistry. In the first place, he had to organise the laboratory and make arrangements for experiments with plant culture in accordance with modern methods, and then he elaborated minute directions for the analytical work in the different chemical stations of Sweden, of which he was inspector. He was consulted in all questions of importance concerning agricultural or technical legislation, and his decision on such questions was always founded upon exact and original experimental investigation, as will be found from his reports upon the analysis of butter and of milk, or his examination of the lactocrite method, and the efficiency of the different mechanical methods of separating the fatty matter from milk, or his investigation in reference to urban sanitation.

It could hardly be expected that, in addition to this official work, he could find time and opportunity for experimental scientific investigations in agricultural chemistry, nevertheless, there are not less than 57 separate papers upon such topics published by him in the *Journal* of the Royal Academy of Agriculture.* I must confine myself here to mentioning only two or three of these investigations.

In the first place, both on account of the intrinsic value of the analytical work bestowed upon the subject, and on account of its practical importance, his treatise on the possibility of introducing the culture of the sugar beet into Gothland must be mentioned. The climate and the arable land of Gothland are in themselves favourable to the culture of this plant, as pointed out long before by A. Müller and others. More than 30,000 hectares, or about one-ninth of the area of this island, consist of almost sterile swamps, the soil being composed of a thin layer of humus formed by decayed vegetable matter which has grown in the stagnant water in the hollows of the plateau of Silurian limestone forming the geotectonic framework of the island.

Nilson proved by chemical analysis as well as by cultural experiments, that the black soil of these swamps is unusually rich in lime and nitrogenous humous substances, containing as much as 4 or 5 per cent. of nitrogen. The sterility of the soil in its natural state is due to the almost total absence of phosphoric acid, and, in some measure, also to the scarcity of potassium. If this want is supplied by artificial

* See *Kongl. Landtbruksakademiens Handlingar och Tidskrift*, 1883–1898.

manuring, the richest crops of corn, rape, and sugar-beet can be obtained. The intelligent farmers of Gothland, to their great economic profit, hastened to follow Nilson's advice ; the barren ground of the swamps is now drained and sown with corn and rape, and, to some extent also, with sugar-beet.

An indispensable condition for maintaining a rational culture of the soil is to have a supply of natural or artificial calcium phosphate. The annual import of phosphates into Sweden is equivalent to more than 18 million kilograms of phosphoric oxide, whilst only 2 or 3 million kilograms are produced in the country, the condition of things not being favourable for the manufacture of basic phosphate. In the Northern provinces of Sweden, especially in the great iron-ore district of Gellivara, apatite occurs so intimately mixed with iron ore, that the latter must be separated from it either by washing or by magnetic extraction. It occurred to Professor J. Wiborgh that the apatite powder could be converted into tetraphosphate by ignition with alkali. When the first experiments had proved successful, Nilson, at Wiborgh's request, took over the analytical investigation and biological experiments with the new fertiliser. Thirty parts of soda are heated to about 900—1000° with 100 parts of powdered apatite, which, on the average, contains about 17 per cent. of felspar.*

The chemical reaction is :

1. $CaFl_2,9CaO,3P_2O_5 + 3Na_2O,CO_2 = 2Na_2O,10CaO,3P_2O_5 + 2NaFl + 3CO_2$.
2. $K_2O,Al_2O_3,6SiO_2 + 2Na_2O,CO_2 = K_2O,2Na_2O,Al_2O_3,6SiO_2 + 2CO_2$.

The product, which consists of neutral silicates and tetraphosphates of calcium, sodium, and potassium, is insoluble in water, but is still assimilable by plants more completely than ordinary tetraphosphate obtained by the Thomas-Gilchrist method. For the manufacture of Wiborgh phosphate a great industrial establishment is now in working at Luleå.

Nilson was a member of the Chemical Societies of England, France, and Germany, and of nearly all learned Societies and Academies of the Scandinavian countries. He was a most active and influential member of the Royal Academies of Science and of Agriculture in Stockholm, but as much as possible avoided representative duties, declining, for example, much to the disappointment of his colleagues, to undertake the Presidency of the former. He was not a brilliant lecturer, but no one was listened to with greater attention.

* The presence of silicate—as might be foreseen from the recent researches of Wagner and others—is essential for the assimilability of the tetraphosphate by plants.

In the scientific world, it awakened not a little surprise commingled with regret that Nilson, in 1883, a few years after his discovery of ytterbium and scandium, left his work in the field of theoretical chemistry, where he had met with such brilliant success, in order to take up the seemingly modest occupation of an agricultural chemist. His friends knew that this involved a great sacrifice on his part, but they felt no astonishment at his resolution. They knew that with Nilson the sense of duty was paramount, and the desire of success of secondary importance. His country needed him to fill that place—that was all. Besides, there dwelt within him an innate love of living nature; he liked not only to study the abstruse problems of natural science, but he was also an admirer of nature herself. He was fond of farming and gardening; he loved flowers, and had a singular talent for arranging them. In this art he considered his own taste infallible, he could admit the talent of others, but he acknowledged the superiority of none. I can see him on one of those days when he had invited a party of friends to his hospitable house, entering the room with a huge burden of flowers from the meadow or garden, arranging them deliberately in his own original fashion, before he came forth beaming with pleasure to welcome his guests.

The burden of labour which his excellent constitution had long sustained without any sign of giving way, at last became too heavy even for his powers. His friends felt anxious, but Nilson showed no anxiety; his trustful sanguine temperament, which, throughout his life-time made him look upon every event from its hopeful side and upon every man from the best side of his character, obscured from his eyes the approach of death, and let the forebodings which inevitably precede it pass by unheeded. He was spared from long lingering and suffering. There was a sudden blow, a short struggle, and all was over.

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